DISSOLVED ORGANIC CARBON AND COLOUR DYNAMICS IN DRAINED AND RESTORED BLANKET PEAT

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The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others.

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ABSTRACT

Peatlands are important terrestrial stores of carbon and a principal source of dissolved organic carbon (DOC) to the fluvial environment. Whilst often regarded as a net carbon sink, enhanced DOC concentrations and an associated rise in the level of water discolouration observed in many artificially drained peatland catchments across Europe and North America suggests that continued degradation may shift the balance of the carbon budget, such that they become a net carbon source. Peatland restoration, in the form of drain blocking, is currently being undertaken in a number of these locations. However, a great deal of this work has been carried out on a pragmatic or even an ad-hoc basis, with a distinct lack of process-based assessment. Thus, very little is known about how such changes in land management affect DOC and colour dynamics. In order to bridge this knowledge gap, this thesis examines a range of processes known to influence DOC/colour production and release. A variety of field monitoring and laboratory measurements were undertaken to assess the upland blanket peat within the Oughtershaw Beck catchment in the Yorkshire Dales National Park, UK.

The installation of drainage ditches was found to reduce both the carbon storage potential of the peat and the quality of upland catchment waters. Drainage lowered the depth of the water table across the peat by an average of 10 cm, enhanced the rate of microbial activity by 33 % and increased DOC and colour production in soil water solutions by 35 %, relative to an adjacent intact site that had not been drained. The greater level of aeration in the upper peat layers associated with a lowered water table also appeared to reduce the degree of surface saturation and the occurrence of overland flow (OLF), resulting in a greater volume of water being drawn down into the peat body. The reduced saturation levels caused the subsidence and compaction of the upper soil layers, which increased the bulk density and ultimately reduced the degree of macroporosity within the soil. In turn, this is thought to have increased the residence time and surface area over which percolating waters flow, which is likely to have enhanced the degree of interaction with decompositional products, and thus the mobility of DOC/colour.

Drain blocking proved to be a highly effective technique for improving the carbon storage potential of blanket peat and ameliorating upland water quality. Blocking, using regularly spaced peat dams, successfully raised the height of the water table across the peat by an average of 4 cm, relative to the drained site. This increased the level of surface saturation and occurrence of OLF, whilst reducing rates of microbial activity and DOC production by 50 %. However, the volumetric changes associated with drainage appear to have resulted in permanent modifications to the structural and infiltration properties of the peat. Both the water table and the proportion of macropore flow at the drain-blocked site were reduced relative to the intact site, as were microbial activity rates, DOC concentration and colour levels. In addition, DOC composition was markedly different to that produced in the soil waters of both the intact and drained sites. The evidence suggests that a greater volume of percolating water travels through the peat matrix, relative to the intact site, which results in a pore water flushing mechanism and the preferential removal of labile un-coloured DOC components. Furthermore, the lower rate of microbial activity relative to the drained site provides evidence against the commonly quoted hypothesis that an enzyme-latch reaction may be sustained in a peat that has been re-wetted following water table drawdown.

Although there was a strong association between DOC and colour, the relationship varied significantly between peat layers, land managements, and through time. This challenges the use of spectrophotometric analysis as an indirect method of DOC determination in peat soil waters as the use of a single regression equation resulted in the miscalculation of DOC concentrations by more than 50 %, as it failed to account of the fact that the fraction of coloured DOC components could vary significantly due to modifications made to microbial decomposition and mineralisation pathways and hydrological routing mechanisms.

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CHAPTER 1

INTRODUCTION AND OVERVIEW

1.1. INTRODUCTION

Peatlands are particularly unbalanced ecosystems in which the net rate of primary productivity and accumulation of organic material far exceeds the rate at which it is degraded and exported (Frolking *et al.* 2001; Gorham 1991). Consequently, they form an important terrestrial carbon store, with northern peatlands alone estimated to hold approximately 200-450 Pg C (Gorham 1991). These carbon-rich soils are a principal source of dissolved organic carbon to the fluvial environment, the transportation of which constitutes a significant link in the global carbon cycle with the average global riverine flux estimated to be between 1 and 10 x 10^{11} kg C $year^{-1}$ (Hope *et al.* 1994). However, while peatlands are often regarded as a net carbon sink, increasing levels of degradation associated with environmental change could shift the balance of the carbon budget, such that they become a net carbon source. For example, although the release of dissolved organic carbon (DOC) from peatlands is a widespread natural process, in recent years elevated DOC concentrations have been observed across the UK (e.g. Freeman *et al.* 2001a; Worrall *et al.* 2003) and in many other locations throughout the boreal zone including: Nova Scotia (Gorham *et al.* 1986), Labrador (Engstrom 1987), Sweden (Forsberg 1992) and Ontario (Schindler *et al.* 1997).

Excess moisture is critical to the maintenance of peatlands, and they are therefore highly sensitive to changes in hydrology that often occur as a result of climate or land management change; factors which are likely only to intensify in future years (Bragg & Tallis 2001; Heathwaite 1995). Of significant threat to peatland sustainability has been the degradation associated with the installation of open-cut drainage ditches (Holden *et al.* 2004). Drainage has been prevalent in many peatlands across the world, but is particularly common in blanket peats; with the UK representing the largest single global contribution (10-15 %) of blanket peat worldwide (Cannell *et al.*

1999; Milne & Brown 1997; Tallis 1998). Natural blanket peat generally consists of a heavily waterlogged, organic-rich soil, where high water tables often result in over 80 % of runoff being produced as saturation-excess overland flow (OLF) (Holden & Burt 2003c). Consequently, runoff production in undisturbed blanket peat catchments is typically termed "flashy" as they are very productive during storm flow events, exhibiting relatively short lag times between peak rainfall and discharge and thus high storm runoff efficiencies, yet they only provide minimal contributions to base flow (Bay 1969; Evans *et al.* 1999).

Artificial drainage was introduced in UK blanket peats to lower the water table in an attempt to improve the productivity of the land for grazing and reduce downstream flood risk by establishing a moisture deficit. However, in addition to a limited improvement in productivity, several negative environmental impacts have been observed including heightened flood risk and an increased release of DOC (e.g. Conway & Millar 1960; Holden *et al.* 2004; Mitchell & McDonald 1992a; 1995), although some of the flood claims are contested by contradictory results (e.g. Burke 1963; Holden *et al.* 2004; McDonald 1973). A significant increase in the flux of fluvial DOC would mean not only the loss of a valuable terrestrial carbon store, but would also lead to increasing levels of secondary environmental degradation because DOC mobilises metals and pollutants, reduces in-stream light penetration, and has the potential to produce carcinogenic trihalomethane compounds during chlorinated water treatment (Kneale & McDonald 1999). Furthermore, because DOC contains a large proportion of coloured humic substances, increasing concentrations seriously affect water quality in terms of colour, taste, safety, and aesthetic value, as well as significantly altering the acid-base characteristics of the water (Mitchell 1990).

Consequently, many drained peatlands have been targeted for restoration aimed towards re-establishing a naturally functioning, self-sustaining ecosystem and reinitiating the peat-forming processes (Holden *et al.* 2004; Waddington & Price 2000; Wheeler & Shaw 1995). Drain blocking by damming with wooden, plastic or metal sheets or filling the drains with peat or vegetation is expensive and time consuming and so land managers demand to know the value of such activity. Clearly, if blocking improves the habitat and the carbon storage potential, and ameliorates water quality and flood risk then the activity is worthwhile and water companies would happily consider the financial viability of such management schemes, given that water discolouration is a very expensive problem to deal with at the potable water treatment works.

The current re-evaluation of the use of the uplands, including moves to improve carbon storage, preserve biodiversity, rehabilitate surface waters and recreate a natural landscape highlights the need to understand the key processes that may affect the impact of any policy changes and the effectiveness of any rehabilitation programme. However, although recent restoration schemes have pursued drain blocking as a possible strategy for peatland regeneration, there has been a distinct lack of process-based assessment with respect to such changes in land management, and hence very little is known about the influence of either drainage or drain blocking on the mechanisms likely to influence DOC and colour dynamics in blanket peat soils.

The research presented in this thesis has sought to bridge this gap in knowledge by implementing a comprehensive process-based assessment, incorporating both field monitoring and laboratory measurements to evaluate how drainage and drain-blocking influence DOC and colour dynamics in blanket peat soils. It is hoped this method of approach will improve our knowledge of the complex relationships and interplay that exist between the many biotic and abiotic processes controlling DOC/colour production and transportation, which will be of benefit to future predictions made with respect to climate and environmental change scenarios in these valuable upland ecosystems. Furthermore, this research will provide significant insight into the efficiency to which drain blocking can reduce DOC release and water discolouration relative to those sites where drains are left open, which should provide land owners and policy makers with the necessary evidence they require before employing further restoration initiatives in an attempt to improve peatland carbon storage potential and ameliorate upland water quality.

1.2. AIM AND OBJECTIVES

AIM: To provide an intensive process-based assessment to establish the mechanisms involved in the modification of DOC and colour dynamics in a drained blanket peat, and the efficiency to which drain blocking is able to restore them, and consequently the influence of such changes in land management on carbon storage potential and water quality levels, relative to those currently observed in undisturbed blanket peat.

OBJECTIVES:

1. Establish the effect of drainage and drain blocking on the DOC storage potential, within the soil profile of an upland blanket peat.
2. Determine the effect of drainage and drain blocking on the quality and likely treatability of discoloured waters in an upland blanket peat.
3. Assess the spatial and temporal variability of the colour – carbon relationship, and thus the suitability of using colour as a proxy for true DOC determination.
4. Establish the effect of drainage and drain blocking on DOC production potential, within the soil profile of an upland blanket peat.
5. Determine the effect of drainage and drain blocking on the principle hydrological controls of runoff production, and thus DOC and colour transportation, within the soil profile of an upland blanket peat.

1.2.1. DETAILED EXPLANATION OF AIM AND OBJECTIVES

Aim: To provide an intensive process-based assessment to establish the mechanisms involved in the modification of DOC and colour dynamics in a drained blanket peat, and the efficiency to which drain blocking is able to restore them, and consequently the influence of such changes in land management on carbon storage potential and water quality levels, relative to those currently observed in undisturbed blanket peat.

DOC and colour dynamics are controlled by a number of interacting environmental factors that influence rates of production, mobility and export. Biological processes, such as the rate of decomposition, primarily control the production of DOC and colour, whilst abiotic factors (e.g. hydrology) control their export (McDowell & Likens 1988). Specific mechanisms known to influence DOC and colour dynamics include water table depth and moisture content (Mitchell & McDonald 1992a); enzyme activity (Freeman *et al.* 2001b); soil structure (Holden *et al.* 2001; Jardine *et al.* 1990b); runoff regime (Pastor *et al.* 2003); and organic matter content (Hope *et al.* 1997).

Drainage and drain blocking has undoubtedly modified some of these mechanisms. It appears the elevated levels of DOC and water discolouration observed in drained peat catchments (e.g. Mitchell & McDonald 1992a; 1995) have occurred because the water table drawdown associated with drainage affects the preferential flow path through the peat body, which may in turn alter certain physical, chemical, biological and hydrological properties. However, the degree to which they interact and are modified is poorly understood. It is therefore the aim of this thesis to provide a comprehensive process-based assessment, incorporating both field monitoring and laboratory measurements to determine how the installation of drainage ditches and the current restorative practice of drain blocking influence the mechanisms responsible for DOC and colour dynamics in an upland blanket peat soil. The main processes investigated are categorised into two principle components:

1. **DOC and Colour:** Monitoring DOC and colour levels within the three land managements; Examining DOC/colour transportation over and within the soil profile; Assessing the relationship between DOC and water colour; Measuring enzymatic activity and organic matter content and inferring DOC production.

2. **Runoff:** Monitoring water table depth and variability; Measuring proportions of surface and subsurface flow; Identifying structural and infiltration changes, such as bulk density, macroporosity and hydraulic conductivity.

Concentrating on the variables in such a manner provides an improved understanding of the interplay between the varying mechanisms, which is imperative if accurate predictions are to be made about the influence of future climate and environmental change scenarios on carbon losses and water quality from blanket peat ecosystems.

Objective 1: Establish the effect of drainage and drain blocking on the DOC storage potential, within the soil profile of an upland blanket peat.

It has become increasingly apparent that the degradation of an important terrestrial carbon store and the associated ecosystem destruction observed in drained blanket peat is not desirable, which has resulted in increasing levels of protection for undisturbed sites and restoration for those that have been damaged. For example, the installation of drainage ditches has been shown to increase the release of DOC to the fluvial environment (e.g. Mitchell & McDonald 1992a; 1995; Worrall *et al.* 2003). However, these studies often only monitor water colour and use this as a proxy for actual DOC determination, and they generally monitor drainage water rather than the soil water solutions. In addition, the effects of peatland restoration on DOC dynamics are very poorly understood, with only a few studies undertaken in this area (e.g. Glatzel *et al.* 2003; Wallage *et al.* 2006; Worrall *et al.* 2007b) and with contradictory results already prominent.

Therefore, Objective 1 is fundamental in that it i) establishes the principal differences in actual DOC concentrations, and therefore likely carbon storage potential between undisturbed and drained blanket peat; ii) determines whether restoration in the form of drain blocking is a successful technique for reducing the release of carbon via DOC and thus helping to revert the ecosystem back to a net carbon sink; and iii) is a prerequisite for identifying the likely processes responsible for alterations to DOC release between land managements, that are investigated in the following objectives.

Objective 2: Determine the effect of drainage and drain blocking on the quality and likely treatability of discoloured waters in an upland blanket peat.

DOC is also an issue for the water industry, as most of the UK's upland peats are located in major water supply catchments. Increased fluvial DOC causes problems in the production and distribution of drinking water as it significantly deteriorates water quality, particularly in relation to water colour, and the removal of DOC is often the most expensive operation in terms of water treatment for if it is not completely removed the water supply will have low residual chlorine (bringing limited protection against biological contamination); potential for the formation of disinfection by-products; and will exhibit low aesthetic quality (Worrall *et al.* 2003).

Little is known about the effect of drain blocking on the production of discoloured water and its likely treatability and removal at the potable water treatment works, compared to waters sourced from undisturbed or drained blanket peat. Although conventional methodologies have generally been content with simply quantifying the relative changes in the level of water discolouration in response to environmental change (e.g. Forsberg 1992; Watts *et al.* 2001), there is a need to investigate the quality of discoloured water by quantifying changes in the composition of DOC.

Changes to the character and speciation of DOC will ultimately alter the proportion of labile to refractory compounds and thus the bioavailability and reactivity of DOC, which would undoubtedly influence not only the way that DOC is transferred through the global carbon cycle, but also the ability to which water colour is removed and disinfected at the water treatment works. Thorough characterisation is a complex task requiring a hierarchical analytical approach, which is time consuming, labour intensive and expensive. Given the number of samples collected, such a rigorous approach was deemed to be beyond the scope of this project. Thus, Objective 2 involved a qualitative assessment of DOC composition using spectrophotometric techniques to determine the humic – fulvic (E4/E6) ratio and colour – carbon (C/C) ratio, in order to discriminate between DOC fractions and to differentiate between refractory and labile components, and thus the likely treatability of waters extracted from the varying land managements.

Objective 3: Assess the spatial and temporal variability of the colour – carbon relationship, and thus the suitability of using colour as a proxy for true DOC determination.

A strong linear relationship between DOC concentration and water colour is often reported from peatland waters, and as water colour can be measured easily and at minimal expense a colour – carbon relationship is often used to predict DOC flux based solely on water colour measurement (e.g. Dobbs *et al.* 1972; Mattson *et al.* 1974; Moore & Jackson 1989; Moore 1987; Tao 1998; 2005; 2004; Worrall *et al.*

2002; 2003; 2004). This is despite DOC being one of the simplest and most important determinations in organic geochemistry and which can be measured to within ± 0.1 mg C l^{-1} by processes such as oxidation to CO_2 in a combustion-infrared analyser (Clesceri *et al.* 1998).

Objective 3 was concerned with determining whether the process modifications brought about by changes in land management, in conjunction with seasonal variation, were influential in the intrinsic relationship between DOC and water colour and thus assess the suitability of using such a technique to accurately monitor and predict DOC release for fluvial carbon budget research.

Objective 4: Establish the effect of drainage and drain blocking on DOC production potential, within the soil profile of an upland blanket peat.

Evidence about the role of water table drawdown on DOC production and export has provided contradictory results and generally lacks any process-based assessment to support findings. For example, some studies have observed an increase (Tipping *et al.* 1999), some a decrease (Clark *et al.* 2006; Freeman *et al.* 2004a), whilst others have observed no significant change (Blodau *et al.* 2004) in DOC concentrations. In some cases artificial drainage results in a prolonged period of water table drawdown, which increases the level of oxygenation within the peat body. Increased oxygenation has been shown to stimulate the activity of phenol oxidase enzymes resulting in the subsequent removal of inhibitory phenolic compounds, which allows for enhanced decomposition by pivotal degrading hydrolase enzymes and thus increases the amount of labile DOC in the peat body (Freeman *et al.* 2001b).

The rewetting of the peat following drain blocking may not necessarily reverse this process as the loss of phenolic compounds means it is possible for decomposition to continue at depth even after the water table has been restored; a process that has been referred to as the 'enzyme-latch' mechanism (Freeman *et al.* 2001b). However, as of yet there is no evidence to confirm either of these hypotheses. Thus, Objective 4 aims to establish whether changes in land management bring about any variations in the potential production of DOC by measuring the activity of pivotal degrading enzymes.

Objective 5: Determine the effect of drainage and drain blocking on the principle hydrological controls of runoff production, and thus DOC and colour transportation, within the soil profile of an upland blanket peat.

The dominance of water flowpaths in peat varies depending on water table depth in conjunction with antecedent conditions and topographic position (Wallage *et al.* 2006). Therefore, water table disturbance in the form of drainage or drain blocking could also significantly alter the hydrological routing of water through and across the peat, such that runoff production processes are modified and alternative sources of DOC/colour are made accessible. To date however, the monitoring of drained and restored blanket peat has failed to consider the likely changes to the soil structure and the hydrological routing within the soil body that may have developed since drainage installation.

Although saturation-excess OLF is the dominant runoff production process in blanket peat soils (Holden & Burt 2003c), macropore flow has been shown to be an important component of subsurface flow in undisturbed blanket peat (Holden *et al.* 2001). However, it is currently unknown whether drainage or drain blocking has any influence on this important through-flow process. Thus, the aim of Objective 5 is to determine whether the greater level of aeration associated with a lowered water table in drained and restored peat changes the soil structure in any way that would likely influence the volume of saturation excess OLF produced, as well as the distribution of subsurface flow, and thus modify the DOC/colour export within/across the peat.

1.3. APPROACH AND METHODS

Historically, peatland research has been limited by both the logistical difficulties of obtaining data from remote upland environments and by the technical difficulties associated with plot-scale and hillslope-scale investigations. Thus, most research associated with the drainage of peatlands has taken a "black-box" approach, focusing on issues of quantity in relation to flood risk and water resources, rather than providing any measurement of the intimate processes likely to be involved.

In response, this thesis has taken an intensive, process-based approach, based at the sub-catchment and hillslope scale to improve the current understanding regarding the individual physical, chemical, biological and hydrological properties that are affected by drainage and drain blocking. This intensive scale of approach is necessary in order to highlight the main processes involved, which are so often overshadowed by the inherent complexities that can occur within an extensive catchment-scale approach. Furthermore, such an approach is more likely to produce a case study example that has potentially national and global applications with respect to limiting the flux of DOC from a valuable carbon storage and ameliorating upland water quality.

In order to fulfil the aim and objectives set out in Section 1.2, the investigation has concentrated on several key mechanisms intrinsically linked to DOC and colour dynamics (as detailed in Figure 1.1 and Section 1.2.1.). Objective 1 investigated issues relating to DOC concentration, whilst DOC composition (E4/E6 ratio; C/C ratio) and water colour levels were covered in Objective 2. Objective 3 monitored the intrinsic relationship between DOC and colour, whilst Objective 4 measured DOC production potential via microbial activity, organic matter content and soil moisture levels. Runoff production and hydrological controls including water table depth, bulk density, degree of macroporosity, hydraulic conductivity and OLF generation were investigated within Objective 5

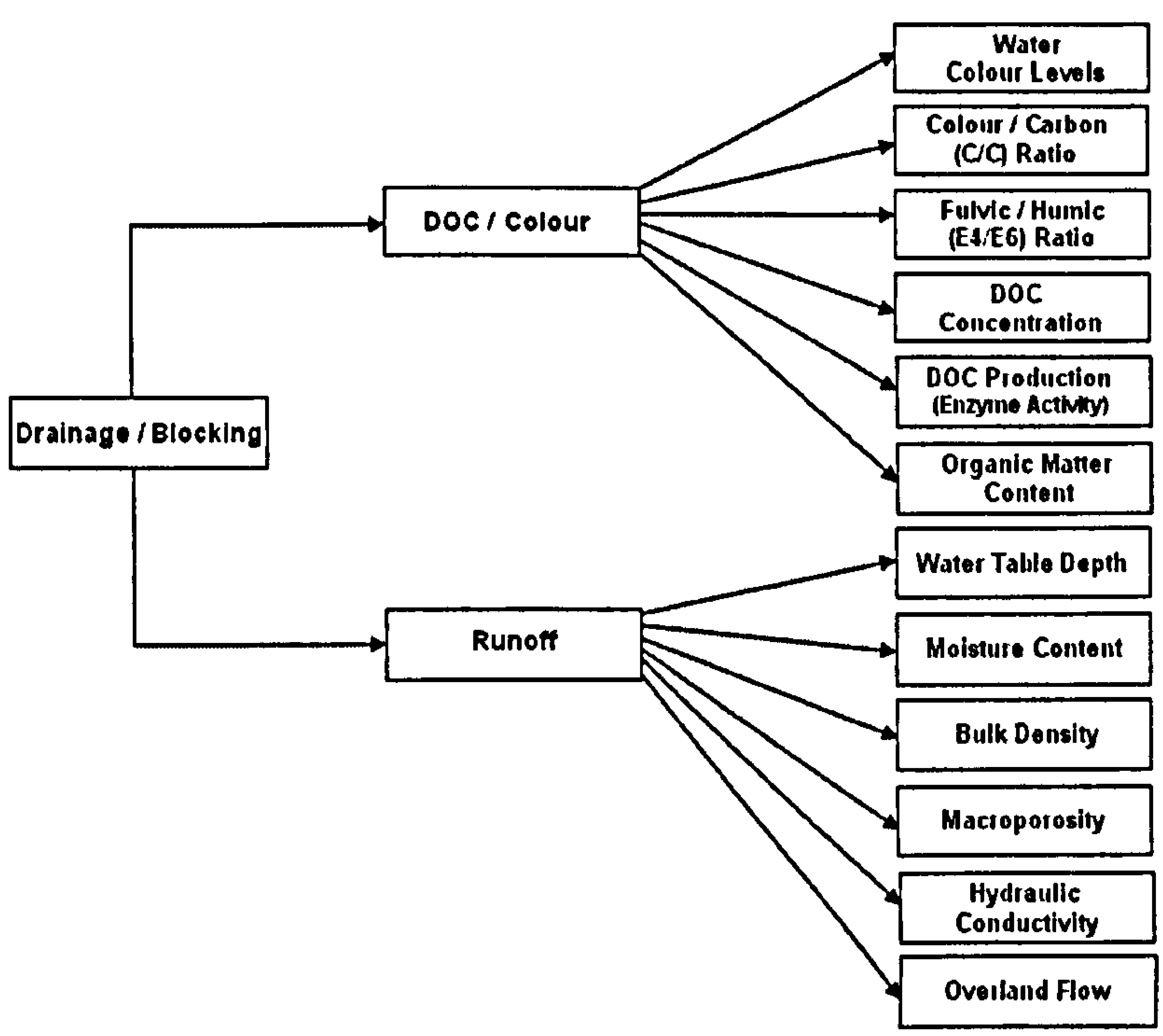

Figure 1.1 Flow diagram summarising how DOC and colour dynamics were investigated.

1.4. THESIS STRUCTURE

To set the national and global context of this thesis and provide a structured case and rationale for investigation, Chapter 2 provides a comprehensive review of peatland ecosystems with respect to development and location, carbon storage potential, DOC, hydrology and water resources, peatland drainage and restoration schemes. Chapter 3 introduces the case-study field site – the Oughtershaw Beck catchment, and details its location and characteristics. It also gives justification for the individual 'treatment' site selection, as well as a detailed description of the site set-up and an overview of the various experimental techniques implemented to fulfil Objectives 1-5. Chapter 4 incorporates Objectives 1 & 2 and provides an assessment of the variability observed in DOC concentrations and the level of water discolouration in soil water solutions extracted from the three land managements (intact, drained and blocked), which includes an expansion of the results that were published in *The Science of the Total Environment* in August 2006. Chapter 5 concentrates on Objective 3 and the intrinsic colour – carbon relationship observed in peatland catchments and evaluates how factors such as varying land management practices and seasonality influence the nature of the relationship, and it also provides a critical assessment of the suitability of using spectrophotometric methods as a proxy for true determination of DOC. Data from a pilot study to assess whether drainage and drain blocking affect the level of enzymatic activity and therefore DOC production within the soil profile (Objective 4), and whether this can be linked to the variability observed in DOC and colour values across the three treatments is covered in Chapter 6. Chapter 7 addresses Objective 5 and analyses how the main hydrological controls and runoff production processes, such as water table depth, macroporosity and hydraulic conductivity, vary between treatments and also assesses their influence on DOC/colour production and transportation. Chapter 8 brings together the findings of the preceding four chapters and provides a summary of the main impacts of drainage and drain blocking in an upland blanket peat on DOC and colour dynamics, and identifies relevant areas for future research.

CHAPTER 2

NATURAL PROCESSES AND ANTHROPOGENIC INFLUENCES ON DOC AND COLOUR DYNAMICS IN BLANKET PEAT SOILS

2.1. PEATLAND DEVELOPMENT AND LOCATION

The amount of organic matter available to a soil is primarily controlled by its rate of accumulation and decomposition within the system, which are themselves primarily determined by the position of the water table and the ratio of aerobic to anaerobic conditions and thus microbial activity (Clymo 1983; Ingram 1983). Under "normal" soil forming conditions, accumulation and decomposition rates are generally in balance so that organic matter neither accumulates indefinitely nor disappears entirely. However, in waterlogged soils where the water table is high, anaerobic conditions predominate and prevent the natural decomposition of plant detritus, resulting in the accumulation of organic matter. As deposition continues, the organic material becomes the growing medium for the vegetation, with the near-surface layer (rooting zone) being subject to decomposition, but with organic material constantly being added due to the roots of the plants growing on it (Tarnocai & Stolbovoy 2006). As more organic material is accumulated, the underlying soil layers are submerged below the water table and the material is no longer subject to significant decomposition (Tarnocai & Stolbovoy 2006). It is in these conditions that peat slowly develops through time from the decay of the vast amount of organic matter that has accumulated in the saturated, anoxic conditions. Such conditions, and therefore peatlands, tend to dominate in upland areas of temperate and boreal zones that experience precipitation-excess or lowland areas where shallow gradients, impermeable substrates or topographic convergence maintain saturation (Holden *et* *al.* 2004).

The majority of peatlands are located in the Northern Hemisphere, with Europe (including the former Soviet Union) and North America being the most significant continents in terms of the absolute extent of peatlands (Charman 2002; Gore 1983). Although the distribution of the world's peatland resources is not known with any degree of accuracy it is thought to be somewhere in the excess of 400 million ha (Charman 2002). Britain's humid climate makes it ideally suited for the development of peat, and thus approximately 2.9 million ha (13 %) is covered in peat, of which 2.6 million ha is located in Scotland (Milne & Brown 1997). Peat is defined in England and Wales as a deposit of at least 30 cm depth, which contains more than 50 % organic carbon (Johnson & Dunham 1963). However, this is not a completely satisfactory definition because peat soils vary significantly according to the nature and amount of organic matter that they contain and the stage of development that they have reached.

The genus *Sphagnum* is one of the most important groups of plant species sequestering carbon in temperate and northern bog ecosystems because *Sphagnum* produces material that is rich in phenolics and is therefore far more resistant to microbial decomposition than the litter of vascular bog plants (Berendse *et al.* 2001). Furthermore, by creating anoxic and acid conditions, *Sphagnum* strongly reduces the microbial degradation of the litter of co-occurring plant species (Berendse *et al.* 2001). Excess moisture is critical to the initiation, development, and maintenance of peatlands, making them very sensitive to variances in water supply (Heathwaite 1995). Both the height and the level of fluctuation of the water table are crucial controls on the vegetational distribution of mires. For example, the lower or more variable the water table, the lower is the cover of *Sphagnum* mosses and the higher the ratio of shrubs to sedges (Stewart & Lance 1983).

2.2. BLANKET PEAT

Peatlands may be categorised in relation to their source of nutrients and water. For example, fens are minerotrophic peatlands that rely on groundwater for water and nutrients, whilst bogs are highly acidic (pH <4), ombrotrophic peatlands that depend on precipitation for water and nutrients (Johnson & Dunham 1963). Generally, ombrotrophic bogs occur only in areas where there is over 600 mm of precipitation per year; however, many blanket bogs in the Northern Hemisphere require precipitation in excess of 1500 mm depending on evapotranspirative losses and topography (Holden 2006). The majority of blanket peats, such as those found in the UK Pennines are ombrogenous due to the high levels of annual precipitation that characterise the region.

Blanket peat soils cover 7.5 % of Britain, and represent the largest single global contribution of blanket peat (10-15 %) (Tallis 1998). They account for 98 % of deep peats (>45 cm) (Milne & Brown 1997), and tend to develop on the gentle slopes of upland plateaux, ridges and benches. The blanket peats of the Pennines, where the high humidity in association the underlying impervious glacial till allow the spread of the mire over sloping terrain, represent one of the largest peatlands in Britain. Blanket peat can cover a variety of landscapes, including slopes and mounds. As such, the definition of peatlands by peat depth (>30 cm) becomes very difficult to apply since peats of 6-7 m may adjoin a relatively thin area of sloping peat *c.*1 m depth, which thins to a variable 25-50 cm peat on a steeper slope (Charman 2002).

2.3. BLANKET PEAT: SOIL PROPERTIES

It is the level of biochemical oxidation (humification) that dictates the individual peat structure, water content and therefore water movement (Holden 2000). Humification occurs throughout the depth of peat; however, it is most rapid in the upper layers due to the relatively high temperatures and oxygen content, which enable the cellulose in organic matter to be broken down faster (Holden 2000). The Von Post scale is the most common method to assess the level of humification in peat, whereby a small amount of peat is inspected and manually squeezed to establish a grading from H1 (completely undecomposed peat, no humification: only clear water emerges when squeezed) to H10 (complete decomposition/humification; no discernible growth structure; peat and water are inseparable). The level of decomposition generally increases with depth.

Peat consists of a mixture of plant remains; therefore it is a highly variable substance (Clymo 1983). Different phases of surface colonisation or local pool development result in a peat of variable properties throughout its profile (Beckwith *et al.* 2003). Thus, some parts of peat hillslopes may be more likely to inherit a heterogeneous peat structure than others depending on local plant or pool occurrences and local drainage (Holden 2005). Blanket peat generally contains very little dry matter because most of its volume is taken up by water, which may be as much as 2,000 % of the dry weight (Prus-Chakinski 1962). Although it is a highly saturated soil with water typically accounting for 90 % of its mass and porosities ranging from 60 % to 90 %, peat exhibits very low hydraulic conductivities (Dasberg & Neuman 1977; Hobbs 1986). The structure, particle size and porosity are primarily controlled by the degree of decomposition as measured by bulk density and fibre content (Boelter 1968). With increasing decomposition, the size of organic particles decreases, resulting in smaller pores and more dry material per unit volume (Boelter 1968).

Saturated peat tends to be 90-98 % water by volume, and even above the water table peat can still hold large volumes of water (approximately 90-95 % water by volume) (Holden 2006). Even small amounts of rainfall are enough to raise the water table, with Holden (2006) finding that the water table rises at a mean recharge rate of 16 mm h^{-1} for a blanket peat in the Oughtershaw catchment, UK. Any change in water table elevation in upper horizons of less decomposed peat represents considerably more water than a corresponding change in deeper, denser peat (Boelter 1964). This is because the peat within the top 50 mm of the profile has four times as much air-space volume (that can be filled with water) as peat at 150 mm depth (Holden 2006).

Boelter (1965; 1968) noted that hydraulic conductivities were highest in upper surface horizons of *Sphagnum* moss peats, whereas deeper, denser peat materials permitted much slower water movement due to their lower hydraulic conductivities. Later, Romanov (1968) developed an idealised two-layered (diplotelmic) peat profile that comprised of a thin upper, "active" layer and a thicker, lower "inert" layer. This was further defined by Ingram (1978) who termed these layers as the "acrotelm" and the "catotelm" respectively. The acrotelm exhibits relatively high rates of hydraulic conductivity and a fluctuating water table, such that it is periodically aerated, and contains a variety of living elements including peat-forming aerobic bacteria, micro-organisms and growing plant material. In contrast, the catotelm is relatively inactive as it is permanently saturated, exhibits lower hydraulic conductivities and is thus devoid of all peat-forming aerobic micro-organisms except for the roots of helophytic angiosperms (Holden & Burt 2003c).

The hydraulic conductivity of peat varies widely in accordance to properties such as: porosity (Baden & Eggelsmann 1963); degree of humification (Baden & Eggelsmann 1963); bulk density (Boelter 1969); fibre content (Farnham & Finney 1965); botanical composition (Boelter 1965); and surface loading (Hanrahan 1954). Thus, hydraulic conductivities vary widely in accordance to the peat type. For example, the lowest values tend to occur in highly humified, structureless *Sphagnum* peats, where small pore spaces and colloidal materials physically and electrochemically impede water movement (Stewart & Lance 1983).

Early work assumed that throughflow in peat was Darcian. However, Burt (1995) and Baird *et al.*(1997) noted that in highly humified peat microbial activity or entrapped air could lead to the blocking of pores, which reduces the ability of peat material to transmit flow, and that larger pore sizes in fibrous peats often generated turbulent flow. Using compressible soil theory, Holden and Burt (2003a) found that for an intact peat there was no significant decrease in hydraulic conductivity with depth, and that the variance within depth categories was similar to the variance between depth categories, indicating individual peat layers cannot be characterised by typical hydraulic conductivity values. For example, for one site at 80 cm depth, hydraulic conductivity varied from 9.70×10^{-8} cm s^{-1} to 6.32×10^{-6} cm s^{-1}. Holden and Burt (2003a) found that large lateral and vertical variances in hydraulic conductivities occurred over short distances, and suggested that this may account for the high frequency of preferential flow pathways within what is otherwise a low matrix hydraulic conductivity peat.

It is only in the upper few centimetres (<10 cm) of the peat mass where hydraulic conductivities are sufficiently high enough to allow rapid throughflow generation through the peat matrix. Thus, it is the low hydraulic conductivity of the peat below 10 cm depth that is largely responsible for the rapid development of near-surface saturation during a rainfall event, resulting in the production of near-surface flow and saturation-excess overland flow (Holden & Burt 2003a).

2.4. BLANKET PEAT: CATCHMENT HYDROLOGY

Hydrology is fundamental to blanket peat development and degradation as it influences gas diffusion rates, redox status, nutrient availability and cycling, species composition and diversity (Holden 2006). In a traditional view first proposed by Alexander von Humbolt (1769-1859), blanket peats were thought to behave like "sponges" by attenuating flood peaks during heavy storms and by sustaining baseflows during drier conditions. However, Burt (1995) noted that most wetlands provide little storage capacity due to their permanent saturation and low hydraulic conductivities. In addition, Evans *et al.* (1999), and Holden and Burt (2003a; 2003c) noted that undisturbed blanket peat at Moor House National Nature Reserve (NNR), northern England, exhibit catchment rainfall: runoff ratios as high as 80 % indicative of the efficient transfer of water from the hillslope to the river channel. Furthermore, Evans *et al.* (1999) noted that runoff production at Moor House was typically flashy with a relatively short lag time between peak rainfall and discharge, and that storm runoff efficiencies were high with values often in excess of 40 %.

Ombrotrophic blanket peat catchments tend to have very flashy hydrological regimes, with stream flows dominated by high peak flows and discontinuous summer flows (Bay 1969; Holden & Burt 2003b). For example, Holden (2006) observed that within the Upper Tees catchment, flows below $0.5 m^3 s^{-1}$ occurred 75 % of the time but this only accounted for 21 % of the total discharge. Undisturbed peat catchments generate little baseflow during dry periods due to a reduction in OLF and throughflow as the water table resides at greater depths within the soil where the rates of hydraulic conductivity are much lower; whilst during rainfall events the water table is able to rise rapidly due to the high specific yield (i.e. the ratio between the quantity of water added to the soil and the subsequent change in the water table) of peat. As the water table rises it enters layers of peat that exhibit progressively greater permeability, which enables water to runoff laterally through the peat at increasingly faster rates and saturation-excess OLF to develop once the water table reaches the peat surface (Bay 1969; Burt 1995; Evans *et al.* 1999; Holden & Burt 2003c). The poor maintenance of baseflow is a major problem for water companies in the UK as during drought periods, reservoirs supplied by upland peats tend to be at risk of severe depletion, despite the relatively large amount of water stored in the peat that covers the catchment (Holden 2006).

2.5. BLANKET PEAT: RUNOFF PRODUCTION PROCESSES

As blanket peat generally consists of an anaerobic, heavily waterlogged, organic-rich soil, the high water table often results in the majority of runoff being produced as saturation-excess overland flow as the soil has only a limited rainfall storage capacity (Holden & Burt 2003c). This results in the flashy hydrological nature that is typical of undisturbed upland peat catchments, as the majority of rainfall is transferred rapidly over the soil surface to rivers and streams. However as seen in Figures 2.1, river flow is actually the product of a range of runoff production processes operating on an individual hillslope-scale.

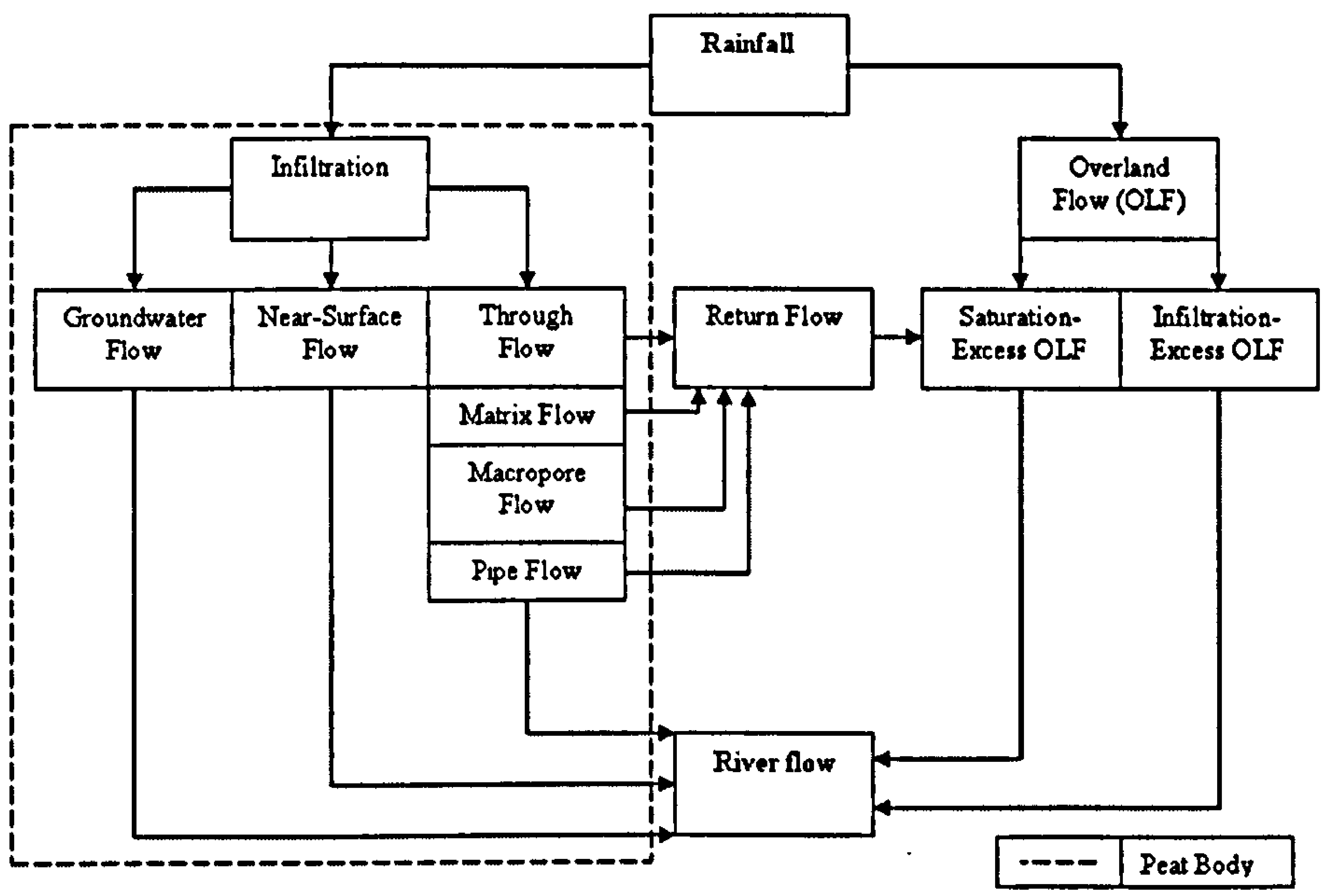

Figure 2.1 A diagrammatic representation of the individual runoff production processes.

The runoff production processes operating in blanket peat soils range in scale from the dominating surface saturation-excess OLF to the rarer infiltration-excess OLF generated during heavy storm events when rainfall intensities exceed the rate at which water is able to infiltrate the soil, through to near-surface and subsurface flow within the soil matrix, within macropores >1 mm in diameter and through larger continuous pores known as soil pipes. For example, Holden and Burt (2003c) noted that at Moor House around 80 % of runoff occurred as satuation-excess OLF, 36 % as macropore flow, 10 % through soil pipes and 20 % was produced as shallow throughflow via the soil matrix. These figures exceed 100 % as runoff processes are not independent from one another, as water travelling over the surface as overland flow at one point may later take the form of subsurface flow through the soil matrix, whilst near-surface flow may later reappear as return flow and combine with saturation-excess overland flow.

The relative importance of these runoff production processes is also known to vary depending on water table depth in conjunction with antecedent conditions and topographic position (Holden & Burt 2003b; Wallage *et al.* 2006). For example, the individual processes act on different spatial and temporal scales, with saturation-excess OLF and sub-surface flow having identical source areas, but their temporal contributions to stream flow are very different as OLF is much faster than throughflow; meanwhile, although satuation-excess OLF and infiltration-excess OLF are both rapid runoff production mechanisms and thus have similar temporal characteristics, their source areas are very dissimilar. The individual runoff pathways (or flowpaths) are important in their own right because they control the volume and rate at which water moves to the stream channel, as well as having an influence on nutrient and sediment content, with water moving through subsurface soil layers tending to have a very different chemistry from that which has moved solely over the soil surface (Burt 1996). For example, OLF and macropore/pipe flow provide rapid hydrological flowpaths and can transport significant amounts of water over and across the soil, yet both processes have limited effect on water quality due to their relatively short contact time with the soil matrix and decompositional products (Jardine *et al.* 1990a; Luxmoore *et al.* 1990). In contrast, water travelling within the peat matrix through smaller meso- and micropores <1 mm in diameter travels at a much slower pace due to the longer, more tortuous flowpaths through the soil body, which also means that these processes have a greater ability to supply solutes to percolating waters as there is greater opportunity for the water to interact with organic material due the greater surface area over which they flow (Jardine *et al.* 1990a; Luxmoore *et al.* 1990).

2.6. BLANKET PEAT: TERRESTRIAL CARBON STORE

Peatlands form an important role in the accumulation and export of organic material and are an important terrestrial carbon reserve (Heathwaite 1995). Carbon occurs in all organic compounds and is fundamental to the structure of all living organisms. As seen in Figure 2.2, carbon is ultimately derived from inorganic atmospheric carbon dioxide that is assimilated by vegetation during photosynthesis (Charman 2002). The accumulation of organic matter from plant detritus in the development of peat has resulted in peatlands storing an estimated 455 Pg C, which represents about 60 % of the atmospheric carbon pool and over one third of the global soil carbon store (Gorham 1991; Immirzi *et al.* 1992). As such, their preservation is of extreme importance in terms of providing a sustainable terrestrial carbon store.

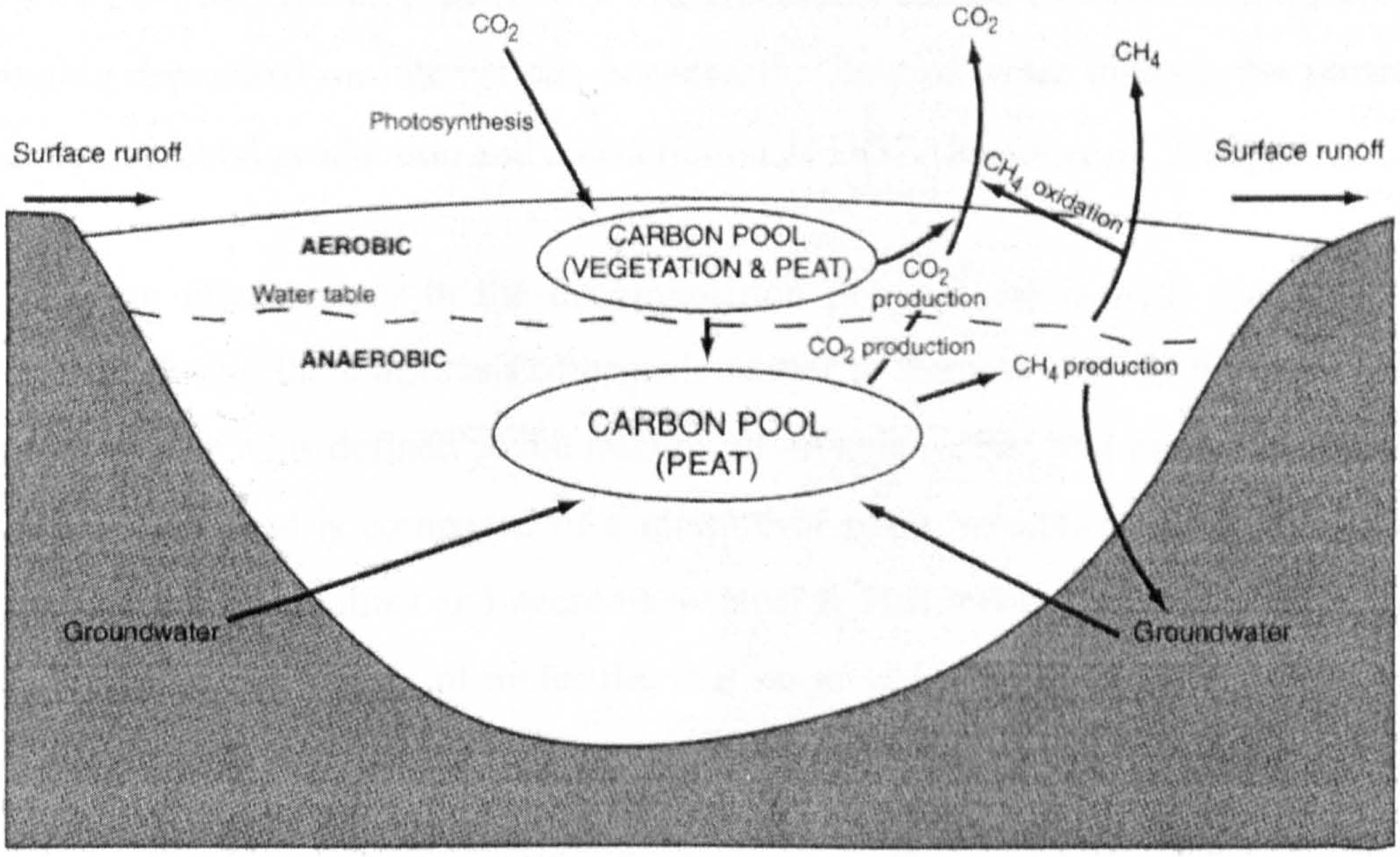

Figure 2.2 A simplified representation of the processes operating in the carbon cycle for a model peat soil, sourced from Charman (2002).

Peatland ecosystems accumulate carbon because annual net primary productivity of the vegetation generally exceeds the annual decomposition rate of litter and peat (Frolking *et al.* 2001). Hence, northern peatlands have been a persistent sink for CO_2, averaging 0.02 to 0.03 kg CO_2-C m^{-2} yr^{-1} over the past 5000-10,000 years, with net carbon accumulation rates in Britain commonly 40-70 g C m^{-2} y^{-1}, which is about 0.5-1.0 mm depth of peat per year (Clymo 1983; Gorham 1991; 1995). Soil organic carbon is in active exchange with the atmosphere, although the relatively large size and long residence time of this pool (in the order of 1,200 yr) make it a potentially important sink for carbon released into the atmosphere by fossil fuel combustion (Post *et al.* 1982). The amount of carbon in the soil is the balance between inputs or organic material from the biota that ultimately depend on the type of vegetation and its productivity at a particular site, and losses primarily though heterotrophic respiration, which depend on climatic conditions such as temperature and moisture (Post *et al.* 1982).

2.6.1. DISSOLVED ORGANIC CARBON

Peatlands are a principal source of dissolved organic carbon (DOC) to the fluvial environment, the transportation of which constitutes a significant link in the global carbon cycle, with the average global riverine flux estimated to be between 1 and 10 x 10^{11} kg C $year^{-1}$ (Hope *et al.* 1994). The amount of carbon exported from peatlands is highly dependent on interactions between the flow of water through the peatland and the microbial production and consumption of DOC (Pastor *et al.* 2003).

DOC is an intermediary in the decomposition process and is both produced and consumed during the diagenesis of organic matter to form the peat sediments (Schiff *et al.* 1998). DOC is defined as the fraction of organic carbon that can pass through a 0.45 μm filter, and is composed of a mixture of plant, microorganisms and animal products from metabolites and necromass (Neal & Hill 1994; Thurman 1985). Thus, DOC consists of a variety of molecules that range in size and structure from simple non-humic acids and sugars to complex humic substances, and therefore contains both biologically available (labile) and more recalcitrant components, neither of which are routinely quantified in freshwater monitoring programmes.

Humic substances are defined as "a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterised as being yellow to black in colour, of high molecular weight and refractory" (Aiken *et al.* 1985). However, humic material cannot be defined in terms of structure or function, as they do not belong to any unique chemical entity (Mitchell 1991). Therefore, they are often defined operationally in terms of their solubility in aqueous solutions. These include fulvic acid, which is soluble in both acidic and alkaline solutions and is light yellow to yellow-brown in colour and has the lowest molecular weight (about 500 to 1500 g mol^{-1}); humic acid, which is soluble in alkaline solutions, but insoluble in acid below pH 2, has an intermediate molecular weight and is dark brown to black in colour (Langmuir 1997); and humin, which is insoluble in acid or alkaline solutions and has the highest molecular weight (Langmuir 1997; Schnitzer & Khan 1972; Thurman 1985).

In contrast, non-humic substances are comprised of relatively simple uncoloured compounds that have definite physical and chemical characteristics, such as carbohydrates, proteins, peptides, amino-acids, fats, waxes and other low-molecular-weight organic substances (Thurman 1985). In general therefore, non-humic substances tend to be degraded at a faster rate than humic substances as they are more readily available and thus easily consumed by micro-organisms and invertebrates compared to the more complex and biologically resistant humic compounds (Schnitzer & Khan 1972; Sposito 1984; Thurman 1985).

Humic substances are generally the dominant fraction in DOC, which results in a strong association between DOC and colour. Consequently, a substantial amount of research into peatland carbon budgets has relied upon the use of colour as a proxy for the true determination of DOC (e.g. Dobbs *et al.* 1972; Mattson *et al.* 1974; Moore & Jackson 1989; Moore 1987; Tao 1998; 2005; 2004; Worrall *et al.* 2002; 2003; 2004). However, the contribution of humic substances to DOC has been found to vary by between 30 and 90 %, meaning that in some circumstances up to 70 % of DOC can be composed of the small, uncoloured non-humic compounds (Thurman 1985; Wallage *et al.* 2006).

Within the mass of the coloured humic substances the fraction of humic and fulvic acids also vary relative to one another. As the ratio of these differently coloured organic compounds varies, the samples will absorb different wavelengths of light and therefore provide different responses in spectrophotometric analysis. For example, humic acids have a greater reddish colour than fulvic acids, and thus have a greater level of absorbance at higher wavelengths in the light spectrum (Thurman 1985). The E4/E6 ratio compares the level of absorbance at 465 nm to that at 665 nm for a given water sample. This can be used to measure the proportion of fulvic acid to humic acid in the coloured humic component of DOC (Thurman 1985). The E4/E6 ratios are higher for fulvic acids (8 to 10) and lower for humic acids (2 to 5). As humic acids are more mature than fulvic acids, the E4/E6 ratio can also be used to measure the degree of humification (Schnitzer & Khan 1972; Thurman 1985).

DOC is of particular significance in peatlands because any change in the flux of DOC will result in a significant regional redistribution of terrestrial carbon. In downstream ecosystems, DOC exerts significant control over productivity, biogeochemical cycles and attenuation of visible and UV radiation (Pastor *et al.* 2003). DOC provides a potential source of carbon for microbial growth and is a powerful agent for the complexation of metals, thus it plays an important role in metal toxicity and metal export (Qualls & Richardson 2003; Tranvik 1992). In addition, DOC has serious affects on water quality in terms of colour, taste, safety, and aesthetic value, as well as altering the acid-base characteristics of soil and streamwater (Mitchell 1990).

Processes generating DOC include the direct leaching of soluble substances produced from plants and litter, exudation of substances from roots, microbial solubilzation of substances originally insoluble, and production of DOC by algae (Figure 2.3). Processes found to consume DOC comprise microbial mineralisation, microbial mineralisation catalyzed by photolysis of DOC to low molecular size compounds, and photochemical mineralisation.

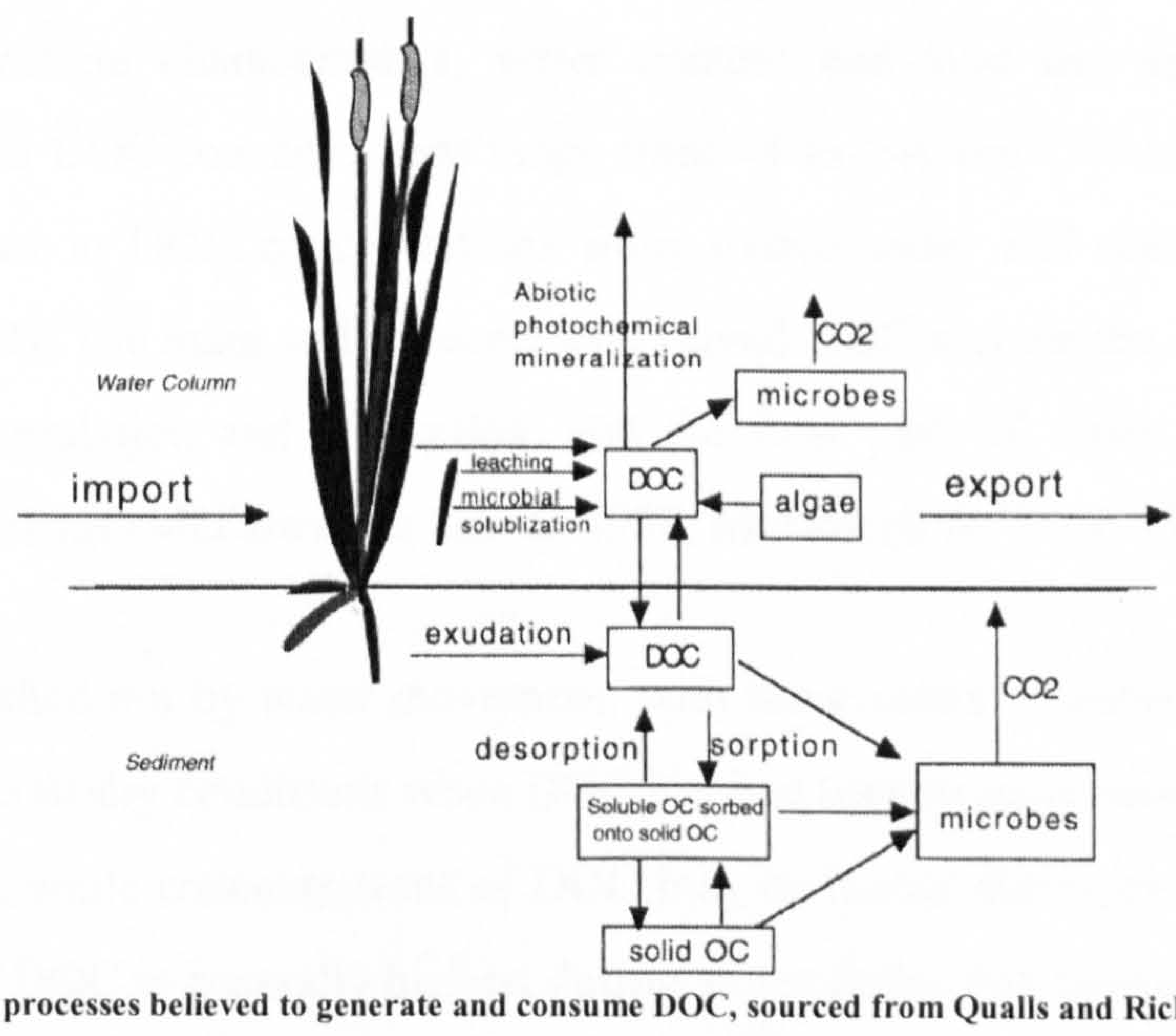

Figure 2.3 The processes believed to generate and consume DOC, sourced from Qualls and Richardson (2003).

Understanding the DOC dynamics of a blanket peat requires knowledge of the controls on the production of DOC, the characteristics that control DOC retention within the soil, as well as the hydrologic pathways within the catchment (Moore 1997). Interstitial soil waters are low in ionic strength and contain low concentrations of inorganic ions (Thurman 1985). Thus, they are able to dissolve organic matter from the litter layer and carry it through the soil layers. The decompositional pathway in peat generally follows a slow change from large to small molecules, with the major constituents of plant and animal material forming the bulk of the peat generally termed humin or humic substances (Thurman 1985).

Schiff *et al.* (1998) found that hydrology governs the appearance of the pore water profiles by controlling both the position of the water table and the velocity of water movement along the various flow paths. They suggested that the flow system affects the supply of labile organic substrates, the supply of redox sensitive species, including the depth of penetration of oxygen, and the flushing of reactants and products. Schiff *et al.* (1998) noted that despite the complexity of the flow systems in peatlands, most models and supporting data show that the flow paths in the uppermost peat layers dominate the hydrogeologic flow in peatlands, meaning that the export of DOC is governed by the processes affecting the uppermost peat layers, despite the large inventory of carbon held throughout.

Many studies have shown a considerable spatial and temporal variation in DOC concentrations in soil water; however identifying such controls is difficult, although temperature, substrate characteristics, water content and land use appear to be important. Fluvial DOC concentrations range from <1 to >40 mg C l^{-1} and generally reflect differences in DOC concentrations from source water and catchment soils (Hope *et al.* 1994). The main soil influences on fluvial DOC include the rate of DOC production, accumulation and adsorption, and the flow path of water through the different soil horizons (McDowell & Likens 1988; McDowell & Wood 1984).

Soil DOC is flushed out by water movement, with the greatest concentrations often following periods of dry conditions when DOC has had time to accumulate (Charman 2002). However, while concentrations of DOC may be higher during periods of low flow, the flux of DOC is generally highest during storm flows. For example, Schiff *et* *al.* (1998) found that approximately 50 % of the total DOC export occurs during the upper 10 % of the flow values, which suggests that many sampling programmes underestimate the total DOC export as they overlook at least some of the high flow events.

Once in the stream channel, many complex physical, biological and chemical processes such as flocculation, biological uptake, precipitation, complexation, respiratory losses and chemical sorption by sediments may modify both the flux and composition of the various carbon fractions, providing a secondary control on the spatial variability of DOC (Hope *et al.* 1994; Meyer & Tate 1983; Thurman 1985). DOC is also continually subjected to in-stream biotic oxidation by micro-organisms and invertebrates, who produce smaller carbohydrates, amino acids and phenolic compounds, which are highly reactive (Dawson *et al.* 2001; Hope *et al.* 1994).

2.7. BLANKET PEAT: UPLAND WATER SOURCE

Peatlands exhibit a rich biological diversity and provide a valuable habitat for flora and fauna. They also form major components in the global hydrological cycle – either as headwaters of complete catchments or as principal factors within catchments and are thus instrumental in the maintenance of water quality and quantity (Charman 2002). UK headwater catchments provide an important element of "environmental capital" in the river system as their naturally high rates of runoff help sustain major water supply schemes and assist downstream dilution of pollutants as well as maintaining freshwater biodiversity (Newson *et al.* 2001).

2.7.1. WATER DISCOLOURATION

Nearly 45 % of Yorkshire Water's public water supply is obtained from direct supply reservoirs usually draining peat, thus water quality poses a significant issue for water management (Butcher *et al.* 1995). The dissolution of organic fulvic and humic substances from direct inputs such as litter residue or from the soil via microbial metabolism, leaching and erosion can present a serious threat to the quality of drinking water. The major impact being aesthetic, as DOC results in the appearance of a yellow-brown discolouration in runoff (Mitchell 1991). However, chlorination to disinfect the coloured waters can also result in the production of trihalomethanes (THMs) such as chloroform, which are suspected carcinogens (Kneale & McDonald 1999). The EC maximum colour standard for treated water is 1.5 au m^{-1} at 400 nm, and treatment undertaken to reduce these impacts involves considerable operational cost, for if it is not completely removed the domestic water supply will have i) low residual chlorine (bringing limited protection against biological contamination); ii) potential for the formation of disinfection by-products; and iii) will exhibit low aesthetic quality (Reynolds *et al.* 1995; Worrall *et al.* 2003).

The discolouration of water supplies from peatland areas is a widespread natural process, and is common throughout many parts of the world, particularly in the USSR, the USA, Canada, Scandinavia and the UK (Forsberg 1992; Mitchell 1990). Water colour is generally assessed using a spectrophotometer, which measures the light absorbance at varying wavelengths. Most water companies in the UK measure absorbance at between 400-405 nm, whereas the UK Environmental Change Network (ECN), who collect various hydrological datasets across the country, uses 436 nm (Sykes & Lane 1996).

Water colour is generally low during the dry summer months and increases rapidly to its annual maxima following the onset of autumn rainfall, with Naden and McDonald (1989) demonstrating that more than 50 % of the variation in runoff colour can be accounted for by soil moisture deficits 3 and 14 months previously, which suggests that peat moisture status significantly influences water colour. The changes in water quality that are often associated with storm events reflect changes in the relative contributions to total discharge from the different hydrological pathways (Cresser & Edwards 1987). The concentration of DOC increases significantly in relation to the amount of water that infiltrates the soil surface and passes through the upper highly organic layers (McDowell & Wood 1984). Thus, both the DOC concentration and the colour of water in upland streams tends to increase substantially during heavy storm events (especially after drought) because water draining laterally through the surface horizons makes a greater relative contribution to the discharge (Cresser & Edwards 1987).

2.8. BLANKET PEAT: DRAINAGE

Peatlands provide a wide range of functions that are essential for supporting plant and animal life and for maintaining the quality of the environment, with blanket peat providing a haven for birds such as red grouse, golden plover, merlin, curlew and snipe (RSPB 2007). Consequently, sporting activities are possibly the most widespread economic use of peatlands, with recreational shooting of wildfowl and other animals very common in both Europe and North America (Charman 2002). However, bogs and moorlands are some of the least productive areas in Britain, with stocking densities of sheep varying from > 1 ewe ha^{-1} on dry hills with thin peat down to 0.25 ewes' ha^{-1} on western blanket bog (Stewart & Lance 1983). Thus, through time many peatlands have become degraded due to the various intensive land management strategies carried out in order to improve productivity and increase revenue, such as peat extraction, agricultural grazing, forestry and land drainage.

2.8.1. HISTORY

Although many European countries such as Holland, Finland, Russia and Ireland have experienced artificial drainage, Britain has been one of the most extensively affected (Baldock *et al.* 1984). Drainage in Britain has been a major factor contributing to the improvement in agricultural productivity since the 1940's. During the "feed-Britain" era after the Second World War, Britain witnessed government grants for expansion in drainage works paid at 70 %, particularly in agriculturally marginal upland peatlands (Holden *et al.* 2006). Although the amount of drainage has been poorly recorded in England and Wales, it is thought that approximately 100,000 ha of blanket peat per year were drained in Britain during the 1960s and 1970s, with suggestions that since the 1940s about 190,000 ha of deep peat (about 9 %) have been drained and forested (Cannell *et al.* 1993; Robinson & Armstrong 1988). By 1980 it was thought the total global area of artificially drained organic wetland soils was nearly 23 x 10^6 ha (Armentano & Menges 1986).

The majority of drainage in England occurred in the northern Pennines and the Yorkshire Dales, and involved the use of apparatus such as the Cuthbertson plough to cut steep-sided, open ditches into wet moorland or blanket bog (McDonald *et al.* 2003). The ditches are normally 40-50 cm deep and spaced 15-35 m apart, and the extracted peat was often deposited upside down in a ridge along the down-slope side of the ditch (Stewart & Lance 1983). In most catchments, the drains usually run along the contour of the land. However, in smaller schemes such as those found in Swaledale and Wharfedale in the northern Pennines, a "herring-bone" pattern was often adopted, which incorporated short lateral feeder ditches that lead into a central collecting ditch (Stewart & Lance 1983).

Artificial drainage was introduced in UK blanket peats to lower the water table in an attempt to improve the productivity of the land for grazing and reduce downstream flood risk by establishing a moisture deficit. However, in addition to a limited improvement in productivity, several negative environmental impacts have been observed including heightened flood risk and an increased release of DOC (Conway & Millar 1960; Holden *et al.* 2004; Mitchell & McDonald 1992a; 1995). A significant increase in the flux of fluvial DOC would mean not only the loss of a valuable terrestrial carbon store, but would also lead to increasing levels of secondary environmental degradation because DOC reduces in-stream light penetration, mobilises metals and pollutants, and has the potential to produce carcinogenic tri-halomethane compounds during chlorinated water treatment (Kneale & McDonald 1999). Furthermore, because DOC contains a large proportion of coloured humic substances, increasing concentrations seriously affect water quality in terms of colour, taste, safety, and aesthetic value, as well as significantly altering the acid-base characteristics of the water (Mitchell 1990).

2.8.2. INFLUENCE ON DOC RELEASE AND WATER DISCOLOURATION

The increasing export of DOC is of international concern as whilst peatlands are generally regarded as a net carbon sink, the increasing levels of degradation associated with environmental change, such as drainage, could shift the balance of the carbon budget, such that they become a net carbon source (Gorham 1991). For example, although the release of DOC from peatland areas is a widespread natural process, in recent years, elevated DOC concentrations have been observed across the

UK (Freeman *et al.* 2001a; Worrall *et al.* 2003) and in many other locations throughout the boreal zone including: Nova Scotia (Gorham *et al.* 1986), Labrador (Engstrom 1987), Sweden (Forsberg 1992), and Ontario (Schindler *et al.* 1997).

In addition, water companies and moorland managers are currently assessing the implications of the EU Water Framework Directive, which requires inland waters to achieve "good ecological status" by 2015 (Holden *et al.* 2007). Thus, significant changes in management practice are required to deal with non-point source pollution, such as discoloured water, and this may have an economic impact on the water industry and be another driver of land management change. As such, it is extremely important to improve our understanding of the processes influencing the release of DOC and discoloured water in order to be able to establish suitable preventative measures for the sustainable management of water resources and quality.

Research investigating the role of lower water tables on DOC/colour production and export are often contradictory, with some studies observing an increase, whilst others a decrease or no significant change. Edwards (1987) and Clausen (1980) both found that drained catchments produced much more discoloured water than those that were un-drained. Edwards (1987) and McDonald *et al.* (1989) noted that after the severe droughts of 1975 and 1976 there was a distinct step-like increase in runoff colour levels in upland Pennine catchments. Colour variability was found to increase and did not return to pre-1977 levels on the cessation of drought. The 1984 drought also resulted in an increase in colour; however, the maximum colour was recorded the following year in 1985. Following this, Naden and McDonald (1989) constructed a 9-year record of water colour from variable frequency sampling at raw water intakes in the Upper Nidd catchment, northern England. Although no overall trend was found, they also identified that the highest colour levels were associated with autumn flushes after summer droughts. Naden and McDonald (1989) concluded that the driest summers had resulted in a water table drawdown that had increased the rate of aerobic peat decomposition resulting in a build-up of colour, which was then available for subsequent flushing in the autumn, although no empirical measurements of these mechanisms were made.

Freeman *et al.* (1993) manipulated water tables on laboratory peat columns collected from a valley bottom wetland in mid-Wales and observed a large increase in DOC in those where the water table was artificially lowered. Furthermore, Mitchell and McDonald (1992a) collected 19 Winter Hill peat samples from intact and eroded sites in the Upper Nidd Valley and subjected them to laboratory simulation of drying and wetting cycles. They found that the length of the drought period was positively correlated to the size of the colour store produced and thus the intensity of the colour flush generated during rainfall simulation. They concluded that chemical and physical hydrophobicity, resulting from excessive soil-water loss ($\geq$ 35 %) during prolonged drought inhibits moisture replenishment and therefore produces a lagged colour flush response in the following autumn. Mitchell and McDonald (1992a) also suggested that the large exposures of bare peat and lowered water table that develop following drainage might increase the total surface area available for severe desiccation and colour production processes to occur. However, they failed to incorporate any measure of *in situ* chemical, hydrological or microbial components, so were unable to confirm their hypothesis and thus the processes responsible for this phenomenon.

Worrall *et al.* (2003) brought together 38 years worth of data for DOC and colour release from three upland peat catchments in the Pennines, northern England. Between 1962 and 2000, they found that for two drained catchments there had been a 50 % and 65 % respective increase in fluvial DOC concentrations, whereas at the third un-drained catchment no significant increase was identified. Worrall *et al.* (2003) suggested that the change in the mode of colour distribution might represent changes in the importance of flowpath mechanisms or changes in the importance of sources within the catchment due to drainage. However, their conclusions were based on statistical assumptions for they were unable to make any empirical measurements regarding the processes involved, such as the level of microbial degradation, or any hydrological measurements such as water table depth or runoff production processes.

In contrast, Moore (1987) and Blodau *et al.* (2004) observed only minor changes in DOC concentrations in drained and harvested bogs, compared with undisturbed peat, whilst Scott (1998) found that although during dry, warm summer months there was increased DOC production, in times of extreme drought, such as 1995, DOC production was restricted. Scott (1998) suggested that this was because an influx of oxygen into the deeper anaerobic layers had altered the decomposition process either by reducing microbial activity due to soil moisture deficit, or by diverting the DOC oxidation pathways of the bacteria towards full mineralization to CO_2. However, Scott (1998) did not perform his analysis on artificially drained peat, nor did he perform any direct measurement of microbial activity or CO_2 production to validate either theory.

A study by Fraser *et al.* (2001) at the Mer Bleue bog Ontario, Canada, found that during the growing season DOC in the upper 0.75 m of the peat usually increased in response to rainfall events, but that DOC did not correlate with water table position. They suggested that this indicated DOC concentrations were dependent on confounding factors such as substrate availability, temperature and DOC partitioning through respiration and methanogenesis. Fraser *et al.* (2001) also provided fluorescence and groundwater data that suggested DOC decreased with peat depth and was attributable to *in situ* microbial consumption of available DOC, and that prolonged drought would reduce the DOC export through the acrotelm and therefore reduce the allochthonous DOC exported downstream, although they performed no measurement of microbial activity or analysis of throughflow processes to confirm this. Chapman *et al.* (1999) recorded lower DOC concentrations in streams flowing through peaty podzols drained for forestry compared with streams flowing through un-drained moorland, and Freeman *et al.* (2004b) subjected a peat in Plynlimon, Wales to a simulated drought of varying duration and observed DOC concentrations were on average 44 % lower than the undisturbed control sites.

Thus, not only has research investigating the role of drainage and a lowered water table on DOC and water colour provided contradictory results, most studies have only monitored the quality of drainage water, rather than the soil solution, and few have linked their measurement to production and transportation processes operating within the soil body. Furthermore, those studies that have monitored processes relating to fluvial carbon export have generally been restricted to forested catchments (e.g. Boyer *et al.* 1997; McDowell & Likens 1988). Therefore it is not known in any detail to what extent and by which mechanism DOC and colour is released and transported in drained blanket peat catchments.

2.8.3. PROCESSES AND MECHANISMS

Silvola *et al.* (1996) noted that the carbon flux from peatlands is closely related to water table conditions, stating that if the water table is lowered the carbon sink-source relationship is likely to be disturbed as a greater percentage of the peat is available for oxidation in biochemical reactions. Thus, it is likely that the rate of peat decomposition and erosion will increase with lowered water tables and effectively more CO_2 and DOC will be available for release (Evans *et al.* 1999; Roulet 1990). In addition, McDonald *et al.* (1991) found that colour is released from peat by a two-stage process i) enhanced bacterial decomposition of organic material during aerobic conditions, leading to an increased availability of humic and fulvic acids; and ii) subsequent washout giving increased water colour.

In undisturbed peat, because the water table remains close to the surface, additional water from precipitation events does not greatly increase the contact with organic rich surface horizons (Schiff *et al.* 1998), although it can link previously isolated wetland pools together, allowing the flushing of accumulated DOC. However, if the water table is artificially lowered (e.g. by drainage), then the greater variability in the depth to the water table associated with precipitation events may permit flow paths to regularly intersect the shallow organic-rich soil horizons. Furthermore, the change from a partially anaerobic to aerobic soil associated with water table drawdown and drainage accelerates the oxidation of stored carbon and its release to atmosphere as CO_2 (Armentano & Menges 1986). Billett *et al.* (2004) suggested that only the shallow (aerobic) part of the peat contributes to stream DOC, and that one of the most important controls on change in the transport of DOC across the soil-stream interface is likely to be the water table position. So, although carbon stored within deep anaerobic peat layers is not a major source of DOC to peatland streams, it does represent a significant potential carbon source that could be mobilised by natural climate or man induced change (e.g. drainage). However, such mechanisms have never been recorded in a drained blanket peat.

If peat is drained and the water table lowered, the surface layers can be irreversibly altered by the formation of an oxidised, dried layer, with elevated organic matter decomposition rates and enhanced nutrient mineralization and release (Ross 1995).

Furthermore, dried peats generally shrink, subside and increase in bulk density, which results in slower hydraulic conductivities. For example, Ross (1995) suggests that the slower hydraulic conductivities of the more humified peat matrix result in longer pore water retention times, allowing greater contact between solutes and peat surfaces, which could enhance chemical and biological DOC processes. However, such hydrological processes have never been monitored in conjunction with DOC or water colour in a drained blanket peat.

Up until the late 1990s the majority of hydrological studies in peatland environments often overlooked the importance of the individual hydrological processes. The studies largely assumed that drainage basins were simple "black-box" input-output systems (Equation 1), in which the headwaters were source areas for runoff, and thus only concentrated on measuring the variability in inputs and outputs, as opposed to "internal" runoff generating processes. For example, most studies have focused on soil water storage, water table height and the development and accuracy of suitable techniques for hydrological measurement as opposed to establishing the effect of processes such as drainage on runoff production mechanisms.

[Equation 1] $$P = Q + E + \Delta (I, R, M, G, S)$$[1]

For example, Conway and Millar (1960) were the first to examine the hydrological effects of drainage. They found that at Moor House NNR, drainage and burning resulted in increased peak flows, reduced lag times, faster return to baseflow levels and lower baseflow levels. Furthermore, they found that the efficiencies of the treated catchments were about 10 % higher than for the untreated catchment. Their water balance approach concluded that intact peats retained significantly more water than drained, eroded or burnt sites. At Coalburn, in Northumberland, Robinson (1986) found that drainage increased peak flows by 10 % and reduced the average lag time by 50 %. However, in contrast to Conway and Millar (1960), Robinson (1986) showed that drainage resulted in a small increase in the annual water yields, largely

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1 P = Precipitation; Q = Runoff; E = Evapotranspiration; I = Interception; R = Surface Storage; M = Soil Water Storage; G = Groundwater Storage; S = Channel Storage (Ward 1975).

through an increase in low flows. Nonetheless, both Conway and Millar (1960) and Robinson (1986) concluded that drains collect and transfer surface water and overland flow before it has time to penetrate into the peat mass or evaporate rather than causing water to be removed from within the peat. However, as they failed to measure the water table or the relative contributions from each of the runoff mechanisms they could not verify their findings.

In contrast, Burke, (1967; 1975a; 1975b) at Glenamoy, western Ireland, and Newson and Robinson (1983) at Rhiwdefeitty Fawr in mid-Wales noted that runoff from drained plots was slower and less peaked than on undrained plots. Burke, (1967; 1975a; 1975b) found that the values of drain flow were always higher than those for surface runoff and assumed this to be a function of soil dewatering, noting there was 23.4 % loss in soil water storage in the drained peat, whereas in the undrained soil there was a 8.6 % increase in soil wetness. Burke (1967) and Newson and Robinson (1983) both noted that in the drained catchments the water table had been reduced, with Burke observing there was also a lot of subsidence attributable to shrinkage caused by the dewatering. Burke, (1967; 1975a; 1975b) found that drain outflow occurred on every day during the 6 year study period, whereas surface runoff occurred on average just over 50 % of the time, and that during heavy rainfall surface runoff from the intact peat was greater than the drain outflow. Both Burke (1967) and Newson and Robinson (1983) concluded that the extra storage created by a lowered water table allowed a greater movement of water into the deeper, less permeable soil horizons, reducing its rate of transmission and therefore moderating stream flow during storm events whilst maintaining flow during drier conditions.

Boelter (1964; 1965) importantly stated that the hydrologic role of any bog depends on the type of peat found in the bog. In addition, soil properties (McDonald 1973) and drainage density (Ahti 1980; Robinson 1986) have also been noted as important factors in determining the effect of drainage on water storage and runoff generation. For example, Boelter (1972) observed that ditches in undecomposed fibric (moss) peats had greater influence on the water table than in more decomposed hemic peats because fibric peats have a higher hydraulic conductivity. Furthermore, Stewart and Lance (1983; 1991) noted that the ditch spacing of 15-35 m at Moor House meant that 85-90 % of the bog was unaffected, whereas Burke (1967) identified that a ditch spacing of 4 m at Glenamoy was required to effectively lower the water table throughout the peat.

The main controversies seen in the results from Glenamoy and Moor House occurred due to a lack of comparability and can be summarised as i) annual rainfall at Moor House is nearly 50 % higher than at Glenamoy, ii) the blanket peat at Moor House is undulating, whereas the Glenamoy bog was smoother and more *Sphagnum*-rich, iii) the hydraulic conductivity at Glenamoy was about an order of magnitude higher than at Moor House, and iv) the drains at Moor House were 15 m apart whereas the drains at Glenamoy were <5 m apart.

Holden *et al.* (2004) summarised the main studies that have taken place concerning the hydrological response of peatlands to drainage (Table 2.1). The majority have been water balance approaches that have presented their results with limited explanation and little or no corroborating field evidence to justify their claims. Often, the different hydrological responses between drained and un-drained catchments were speculatively attributed to the water storage capacity and nature of the ground surface. Such a lack of process-based analysis means that there has been a fundamental inability to incorporate many of the details regarding the hydrological and hydrochemical response of peatlands to drainage.

	Affect on Temporary Storage	Affect on Flood Peak	Affect on Annual Runoff	Quantitative Assessment*	Processes Measured (other than stream flow)	Process Discussion
Lewis (1957)	↓	↑	↑	C	X	Storage
Oliver (1958)		↑		C	X	Storage
Howe and Rodda (1960)		↑	↑	X	X	X
Conway and Millar (1960)	↓	↑	↑	H	X	Storage, Burning
Mustona (1964)		↑		H	X	X
Burke (1967)	↑	↓	↑	H	Water Table	Storage
Howe *et al.* (1967)		↑	↑	C	X	Drainage Density
Baden and Egglesmann (1970)	↑	↓		H	X	Storage, OLF
Institute of Hydrology (1972)		↑	↑	C	X	Storage
Moklyak *et al.* (1975)	↑↓	↑↓	↑↓	C	X	YES - lots
Heikurainen (1968)	↑	↓		H	X	X
Ahti (1980)	↓	↑		H	X	Drainage Density, OLF
Robinson (1980, 1986)	↓	↑	↑	H	X	YES - lots
Newson and Robinson (1983)		↓	↑	C	X	Catchment Characteristics
Guertin *et al.* (1987)		↑		X	X	X
Gunn and Walker (2000)	↓	↑	↑	H	X	Vegetation Changes

Notes. * C = Large catchment data within which some parts of the catchment have been artificially drained, H = small subcatchment or artificially drained hillslope monitored

Table 2.1 A summary of the hydrological effects of peatland drainage, sourced from Holden *et al.* (2004).

Drainage has the potential to significantly lower the water table and shorten the flowpaths from the hillslope to the channel. If drainage is successful in increasing the water storage capacity, then the flood peaks from the hillslope may be attenuated and lag times increased, as more water is able to percolate into the deeper layers of the peat. Over longer periods, however, aeration of the peat will result in an increase in the rate of decomposition of the organic matter, which can be released as dissolved, gaseous and particulate organic carbon (McDonald *et al.* 2003). Not only does this affect the downstream water quality, it also results in subsidence and shrinkage and a subsequent reduction in carbon storage potential of the peat mass itself.

Changes to water flow paths and fluxes across and through the peat may influence how DOC and colour is generated and removed from the soil. Many peatlands have exhibited increases in low flows in response to drainage, which have often been attributed to the slow dewatering of the peat (Burke 1967). Associated feedback mechanisms suggest this is a great threat to peatland development and sustainability (Heathwaite 1995). However, there is currently a lack of knowledge regarding the effect of drainage on the quantity and quality of runoff due to the uncertainties remaining over its control of the water table and water movement through the peat body.

Holden *et al.* (2001) showed that macropore flow was an important feature of blanket peat hydrology and Holden and Burt (2002b) showed that drought could permanently increase macroporosity, the amount of infiltration, and the amount of throughflow. Dried peat generally shrinks, subsides and increases in bulk density, which results in slower hydraulic conductivities. For example, Ross (1995) suggests that the slower hydraulic conductivities of the more humified peat matrix result in longer pore water retention times, allowing greater contact between solutes and peat surfaces, which could enhance chemical and biological DOC processes; however, this has never been investigated in a drained blanket peat.

In addition to increased pore water retention times, cracks (or macropores) frequently open up as the peat surface dries (e.g. Holden & Burt 2002b), and there is the potential that these could permit the rapid movement of water through the upper soil horizons, allowing water to bypass adsorption sites in the lower soil horizons. For example, various studies (e.g. Bevan & Germann 1982; Ross 1995) have shown that the mobility of water and solutes in soils occurs through a complex continuum of pores, which vary in size and shape. Macropores, which hold water under low tensions (~0.3 kPa), have been shown to rapidly transport water and solutes through the soil profile whereas micropores, which hold water under higher tensions (>30 kPa), retain solutes within the soil matrix (Bevan & Germann 1982; Luxmoore 1981). As different sized pores hold soil solution at different tensions, solute concentrations should vary among pore classes because of the various physical and chemical processes associated with the solid-liquid interface. For example, Jardine *et al.* (1990a) found that smaller pores have greater matric potentials and higher solute concentrations than large pores, which results in hydraulic and concentration gradients. Nonetheless, despite the growing awareness of the role that macropores and preferential flow plays in solute movement, their influence on DOC in drained peatlands has been neglected.

Drainage often results in rapid subsidence during the first few years, the rate of which tends to decline after this until it finally adjusts to a more constant value, often controlled by biological oxidation (Lindsay *et al.* 1988). The rate of oxidation depends largely on the final height of the water table relative to the surface as well as climatic conditions. Water table drawdown results in increased loading due to the greater bulk density of the overlying unsaturated peat layers. This results in primary consolidation, as the void spaces within the soil are reduced as the weight of the overburden (now unsupported by water) begins to compress the wet soil beneath (Lindsay *et al.* 1988). Primary consolidation therefore results in soil dewatering as the water is expelled from the diminishing pore spaces.

As the peat dewaters, the reduction in soil moisture makes it susceptible to further "secondary compression". The layers above the water table that have been removed from regular inundation experience physical shrinkage of their structural parts (Lindsay *et al.* 1988), which may result in the collapse of readily drainable macropores (Silins & Rothwell 1998). However, relatively un-humified peat, which exhibits a high proportion of void spaces and thus macroporosity, undergoes a substantial level of primary consolidation and subsidence in response to water table drawdown, whilst more amorphous, humified peat, which has a greater proportion of smaller pores, tends to shrink and crack more because its fibres are not aligned in any way (Hobbs 1986; Okrusko 1995; Ratcliffe & Oswald 1988).

When peatlands are drained, the air-filled porosity of the peat increases and oxygen diffuses rapidly to a greater depth. The loss of water leads to subsidence, and the increased aeration has profound effects on microbial processes (Cannell *et al.* 1993). The lowered water table permits air to move into soil pores, where increased temperatures and oxidation of the peat by aerobic bacteria and enzymes converts the organic components into carbon dioxide, dissolved organic carbon and water, which leaves only the tiny mineral component as residue (Prus-Chakinski 1962). The oxygen halts methanogenesis, but permits aerobic decomposition (oxidation), which occurs at a rate about 50 times faster than anaerobic decomposition (Clymo 1983), increasing the rate of CO_2 carbon loss from the peat and causing further subsidence (Armentano & Menges 1986). As such, shrinkage can be anywhere between 15 and 55 % of the original depth (Prus-Chakinski 1962).

Work by Young (1972) on the Dee catchment showed that peat shrinkage was not effectively reversible because when water was returned to the peat, the peat failed to expand to the same volume as before the water was extracted. This is because once peat dries out, chemical and structural changes cause it to become hydrophobic, meaning it never regains its initial moisture content (Egglesmann *et al.* 1993). This difference in wetting behaviour of dry peat and wet peat may influence the pattern of water movement and therefore water quality in peat.

Although the effect of drainage on runoff production processes has never been fully investigated, Holden and Burt (2002a; 2002b) made some significant discoveries regarding the effect of drought and water table drawdown. For example, Holden and Burt (2002b) noted that the structural changes that occur within peat following drought-induced water table drawdown and shrinkage result in heightened functional macroporosity. They found that this increased the lateral subsurface flow within the peat, and allowed rainfall to infiltrate more readily, to the extent that steady-state surface runoff rates were reduced. In addition, Holden and Burt (2002a) suggested that the removal of vegetation and resultant peat exposure increases the amount of surface desiccation, and thus increases infiltration rates and promotes lateral subsurface flow.

The various runoff pathways attenuate and delay water movement through and across a peatland to differing extents, and also provide individual transport routes for nutrients and sediment (Burt 1996). However, there remains a distinct lack of literature regarding the effect of drainage on the preferential flowpaths in peat, and therefore a fundamental inability to incorporate many of the details of hydrological and hydrochemical responses into runoff models.

In addition to the potential disturbances caused to hydrological pathways and runoff production processes, the oxygenation of previously anaerobic soils may well stimulate microbial and enzymatic activity resulting in an increased production of labile DOC and subsequently the concentration and flux of DOC released (McDowell & Likens 1988; Tipping *et al.* 1997). Field and laboratory experiments by Pind *et al.* (1994) and Freeman *et al.* (2001a; 2001b) indicated that intact peatlands typically exhibit low biodegradation rates because the anaerobic conditions constrain the activity of the enzyme phenol oxidase. Under optimal aerobic conditions, phenol oxidase enzymes break down organic phenolic compounds; however, the anoxic conditions prevalent in peatlands restrict the activity of phenol oxidase, allowing the phenolic compounds to build up. The phenolic compounds inhibit pivotal degrading hydrolase enzymes, such that when the phenolic concentration is reduced, the hydrolase enzymes can freely begin to breakdown the organic material (Freeman *et al.* 2001b). For example, they found that under oxygenation, phenol oxidase activity increased by 700 % relative to anoxic conditions. Such results suggest that the immediate threat of heightened carbon release resulting from increased phenol oxidase activity is most likely to be due to water table drawdown in response to increased temperatures and/or drainage, as opposed to a direct reaction to temperature change. Freeman *et al.* (2001b) summarised this threat as "Oxygen limitation on a single peatland enzyme may be all that prevents the re-release of a major store of global carbon into the atmosphere, with potentially serious implications for future global warming". Potential evidence for such an enzyme latch reaction may be seen in Edwards (1987), McDonald *et al.* (1989) and Watts *et al.* (2001) who all noted distinct step-like increases in colour released from upland catchments, particularly in relation to the 1976, 1984, 1989 and 1995 droughts. However, enzyme activity has never been recorded in a drained blanket peat.

Although there is now evidence to suggest that the oxygenation of deeper peat layers will increase the rate of enzymic activity, it is often assumed that oxygenation will also stimulate an increase in microbial biomass and therefore the amount of enzymes available. However, after a field-based experiment involving water table drawdown in a Welsh peatland, Freeman *et al.* (1996) observed an elevation in enzyme activity without an associated increase in microbial respiration, which suggests that water table drawdown may influence peatland mineralization rates through a direct stimulation of *existing* enzymes, rather than through a generalised stimulation of microbial metabolism.

Hitherto, there has been a distinct lack of literature regarding how drainage affects the processes by which DOC and colour is produced and ultimately transported within the soil profile. The main mechanisms likely to be involved have been summarised in Figure 2.4. Existing carbon balance models for peatlands assume that fluid flow and advective mass transport are negligible at depth (Siegel *et al.* 2002). However, the water table drawdown associated with drainage may result in some distortion of the various hydrological flowpaths. Furthermore, increased oxygenation may trigger an enzyme-latch reaction, which could stimulate enhanced DOC production.

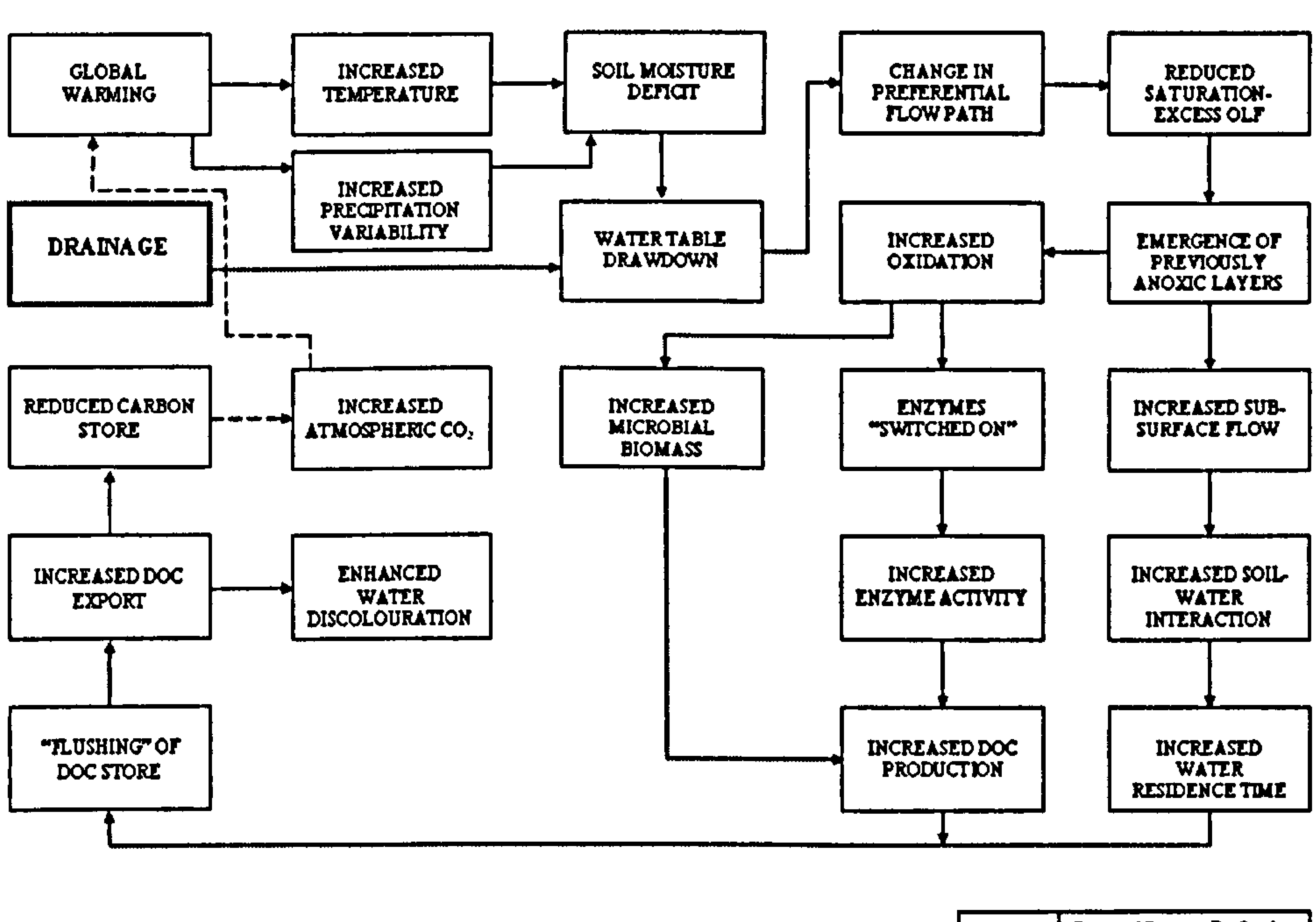


Figure 2.4 A summarised conceptual model of the processes likely to be influenced by drainage.

2.9. BLANKET PEAT: RESTORATION

It has become increasingly apparent that the degradation of an important terrestrial carbon store and the associated ecosystem destruction and deterioration in water quality in drained blanket peat is not desirable, which has resulted in increasing levels of protection for undisturbed sites and restoration for those that have been damaged. Consequently, many drained peatlands have been targeted for restoration aimed towards re-establishing a naturally functioning, self-sustaining ecosystem and reinitiating the peat forming processes (Holden *et al.* 2004; Waddington & Price 2000; Wheeler & Shaw 1995). A significant amount of work toward ecological restoration has taken place in peatland areas but a great deal of this work has been carried out on a pragmatic or even an ad hoc basis, which reflects both the urgency of the requirement to protect important sites, and the frequent shortfalls in available funding (Holden *et al.* 2006).

2.9.1. HISTORY

Some of the first restoration work was carried out in the 1950s in the Netherlands and Germany, but after this peatland restoration remained a relatively minor part of peatland conservation and management until the 1980s (Charman 2002). During the last 25 years, there has been a major increase in interest in peatland restoration, partly associated with a more general rise in consciousness of the need to go beyond preservation to re-creation in conservation (Charman 2002). The short-term (3-5 years) goal is to establish a plant cover composed of peat bog species, with particular attention to *Sphagnum*, and to restore a water regime characteristic of natural peatland ecosystems (Rochefort *et al.* 2003). The long-term (20-30 years) objective is to return the land back to functional peat accumulating ecosystems. European and North American approaches have, however, differed greatly so far because of the different land uses, peat mining methods and goals for restoring regional diversity and cutover bogs have been the main sites where restoration and subsequent research has been focused. Management with respect to drainage and drain blocking is still at an early stage and the results are difficult to assess.

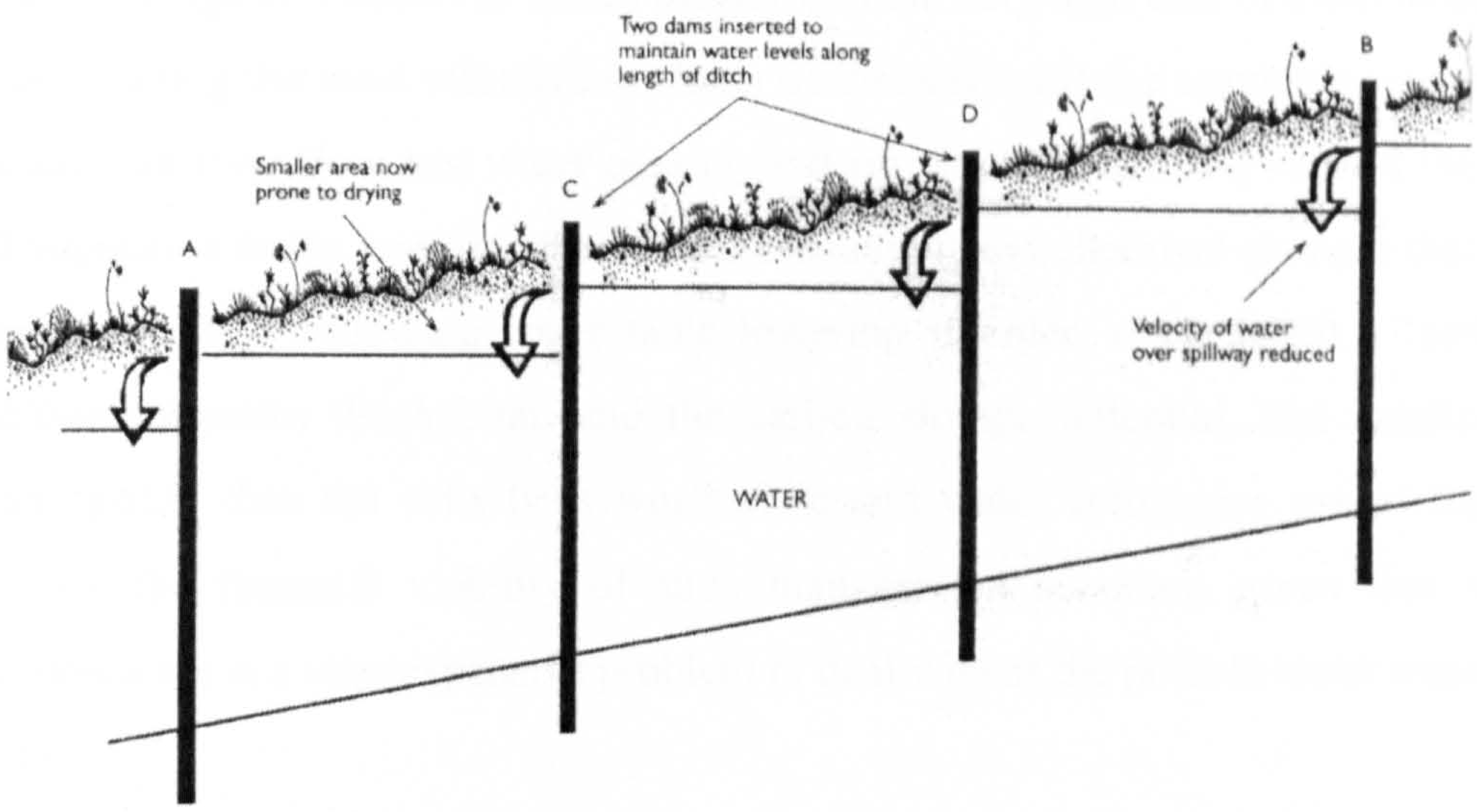


Figure 2.5 Correct dam spacing along a ditch, sourced from Brooks and Stoneman (1997).

Drain blocking is an essential step in controlling water quantity and quality in a drained peatland, and is achieved by damming or infilling drainage ditches, as well as installing bunds to prevent runoff over a wider area. The key objectives are to block the drain via plant recolonisation, raise the water level and ensure the water is of suitable quality (Price 1996). There are hundreds of thousands of kilometres of drainage ditches in the UK uplands, with the average 15 km^2 catchment containing over 200 km of drains (Worrall *et al.* 2007a). There are many techniques that can be used, including sheets of plywood, metal or plastic pushed into the ground across the width of the drain, or dams may be constructed using heather bales, peat, vertical planks or a peat filling between two separate boards. Ideally, blocking should raise the water table evenly over the length of a drain, which involves ensuring that the dams are spaced sufficiently close together where there is any significant angle of slope (Figure 2.5). However, most restoration programmes have been carried out on an ad-hoc basis with many agencies actively blocking drains even though there is little evidence to show it will effectively reduce problems such as elevated DOC removal and water discolouration.

Drain blocking is an expensive and time consuming technique, with plastic dams costing up to £30,000 per km, although peat dams are substantially cheaper at £7,000 per km, thus land managers demand to know the value of such activity (Worrall *et al.* 2007a). Drain blocking has been applied at a wide variety of scales and cost, often without detailed monitoring to assess the effectiveness of the works, and thus there remains a range of unresolved issues including i) the very high cost of ditch blocking; ii) determining the most effective methods of blockage; iii) the uncertain impacts of blockage on river flow and water quality; and iv) the uncertain response of the peat and vegetation in the context of permanent structural and chemical changes that may have taken place following water table lowering (Holden *et al.* 2006). Clearly, if blocking improves the habitat, and the carbon storage potential, and ameliorates water quality then the activity is worthwhile and water companies would happily consider the financial viability of such management schemes, given that water discolouration is a very expensive problem to deal with at the potable water treatment works.

2.9.2. INFLUENCE ON DOC RELEASE AND WATER DISCOLOURATION

Although there have been several investigations into peatland restoration, the majority of these have concerned the cutover bogs of North America and Canada, and very few have assessed the impact of drain blocking on DOC and colour release. Furthermore, within the limited range of research, contradictory results are already apparent. For example, Wallage *et al.* (2006) found that drain blocking was successful in reducing both the DOC concentration and level of discolouration in soil waters compared to drains that were left un-blocked, and that values at the blocked site were lower than those observed for the intact site. They suggested a process of store exhaustion and flushing may operate in blanket peat that has been restored. Wallage *et al.* (2006) also found that drain blocking modifies the composition of DOC, such that darker-coloured humic substances become more dominant compared to the intact site, which implied that there had been a disturbance to DOC production and/or transportation processes. However, no evidence was provided as to which processes were involved. Worrall *et al.* (2007b) performed a modelling experiment at the Trout Beck catchment at Moor House using water colour samples and the colour – carbon relationship to predict the future DOC flux for an un-drained, drained and blocked site. Their results showed that blocking is likely to reduce DOC export by as much as 39 % from a drained peat, although the magnitude of change would be dependent upon the drain-spacing with the greatest improvements seen in areas with high drainage density.

In contrast, Glatzel *et al.* (2003) monitored DOC in soil water solutions in natural, harvested and restored peat bogs in Quebec, Canada. They found that although DOC values were enhanced at the harvested sites, the highest values were observed at a block-cut site where the ditches had been closed to stimulate restoration. Glaztel *et al.* (2003) suggested that the prevention of external drainage to prevent carbon losses by surface runoff resulted in the higher DOC concentrations and enrichment in refractory humic acids at the restored site, although this process was not measured. They concluded that the high DOC concentrations at the block-cut site could be due to either residual DOC accumulation in the un-drained system or preferential DOC release in an anaerobic environment compared to an aerobic one. However, these contrasting results may be a result of the different land management techniques and different peat characteristics.

In addition, Worrall *et al.* (2007a) assessed the short-term impact of drain blocking on DOC and colour production in an upland peat catchment in the Forest of Bowland, northern England. They found that the water sampled from the blocked drains had significantly higher DOC and colour values compared to the unblocked drains, although no discernable change in stream characteristics were observed on the catchment-scale. They concluded that the immediate impacts of drain blocking were to increase water colour and DOC concentrations, suggesting that either DOC that had already been produced under oxidised conditions was still being flushed out by the associated rise in water table similar to that observed in the autumn after a summer drought or there was evidence that an enzyme latch reaction had occurred. Subsequently, it is thought that after the initial flush of DOC from a blocked peat due to disturbance and the enhanced mobility of decompositional products, concentrations may decrease in response to a lower content of potential DOC in the remaining peat. Although Worrall *et al.* (2007a) made no attempt to quantify such a statement in terms of monitoring the levels of organic matter potential or enzyme activity, they did find that blocking successfully increased the water table by 9 cm in the peat adjacent to the drains compared to unblocked drains, and that blocking appeared to successfully restrict drain flow, as flow was only recorded 10 % of the time compared to 81 % of time in unblocked drains.

However, it is felt the results of Worrall *et al.* (2007a) should be treated on the side of caution because of several factors: i) there was a significant influence from both seasonal and periodic (i.e. pre/post blocking) factors on DOC and colour values, and their data suggests there were significant differences (not tested) between the sites before some of them were blocked (i.e. that the drains that were blocked already had higher levels of DOC/colour than those kept unblocked prior to the blocking process being initiated) and it was stated that this difference did not change during the study; ii) DOC was found to be lower at all sites pre-blocking, even at those that were not blocked, compared to those sampled during blocking and post blocking; iii) The reduced levels of flow in the blocked drains could have resulted in the accumulation and concentration of DOC and colour and thus values appeared higher than the open drains where flow occurred more often; iv) Limited pre-blocking data was collected. Sampling only commenced 3 weeks before the drains were blocked, which may have had some effect on the validity of comparisons between sites pre and post blocking. Furthermore, Worrall *et al.* (2007a) suggested that the higher DOC/colour values at the blocked drains could be the result of their sampling strategy, as the drains chosen to be blocked were clearly open along their length while those left unblocked were overgrown and not eroded, and were therefore semi-blocked themselves as opposed to fully functioning drains.

Consequently, as was apparent with studies into the effects of drainage on DOC and colour release, there are major discrepancies as to the effectiveness of drain blocking at enhancing carbon storage potential and improving water quality. It would seem this may be a result of both variability in the individual site/peat characteristics with respect to the initial condition and the type of degradation (cutover vs. drained) and subsequent restoration that was carried out, as well as the type of monitoring and experimental programmes that were performed, most of which were concerned only with ascertaining the impact of restoration on DOC and colour release. Future work may overcome such problems by carrying out intensive process-based research in to the intimate soil mechanisms responsible.

2.9.3. PROCESSES AND MECHANISMS

Understanding and quantifying the impact of blocking on the biogeochemical and hydrological processes controlling DOC and colour production and transportation will provide water-resource managers with the valuable knowledge that is required to proceed with future developments in these sensitive upland catchments. However, to date there has been a distinct lack of research investigating the likely efficiency to which drain blocking can restore these processes.

It appears that blocking alone might not be adequate to achieve the correct hydrological conditions required for vegetation restoration, and that permanent structural and chemical changes may have developed following drainage. For example, Mawby (1995) found, following damming at two sites in Cumbria, north-west England, that although water tables had risen fairly rapidly, they were much more variable than those found in the natural bog surfaces. In addition, for a Canadian cutover bog, Price (1996; 1997) observed that although there were comparable runoff values between the intact and drain-blocked sites, the nature of the storage was very different. Price (1996) found that for a peat that contained blocked drains, the water table fell well below that of a similar intact peat, and suggested this was due to micro-scale changes that had occurred in the soil structure following drainage, which had produced irreversible changes to the way that water is stored. For example, shrinkage, oxidation and compression of the drained peat alter the pore structure of the peat matrix by forming smaller pore spaces, which decrease the plant-available water in the unsaturated zone and increase the variability of the water-table elevation by altering the way in which water is stored (Okrusko 1995; Schouwenaars 1993). Thus, the water table disturbance in the form of drain blocking could significantly alter the hydrological routing of water through and across the peat, such that alternative sources of DOC are made accessible as changes in the hydrophysical peat properties during the restoration process may affect contact time and the area between the solid and liquid phase, which could be an important control on DOC release (Glatzel *et al.* 2003).

Furthermore, the stimulation of phenol oxidase enzymes by oxygenation and the subsequent removal of inhibitory phenolic compounds that allows for enhanced peat decomposition by pivotal hydrolase enzymes may not necessarily be reversed following the rewetting associated with drain blocking. For example, Freeman *et al.* (2001b) suggested that the loss of phenolic compounds caused by the oxygenation associated with water table drawdown means that it is possible for decomposition to continue at depth even after the water table has been restored. A process that has been referred to as the 'enzyme-latch' mechanism; enzymes are 'switched on' by water table drawdown but are then not 'switched off' as the water table recovers. To date, however, this mechanism has not been investigated in a drain-blocked peat.

Figure 2.6 summarises the main chemical, physical, biological and hydrological processes likely to be involved in drain blocking. The main aim of blocking is to increase the height of the water table. This may result in decreased DOC generation due to a reduction in the rate of peat decomposition and desiccation, or it may increase the quantity of DOC released due to the submergence of the heavily desiccated and chemically altered peat, in conjunction with altered preferential flowpaths and continued enzymatic stimulation.

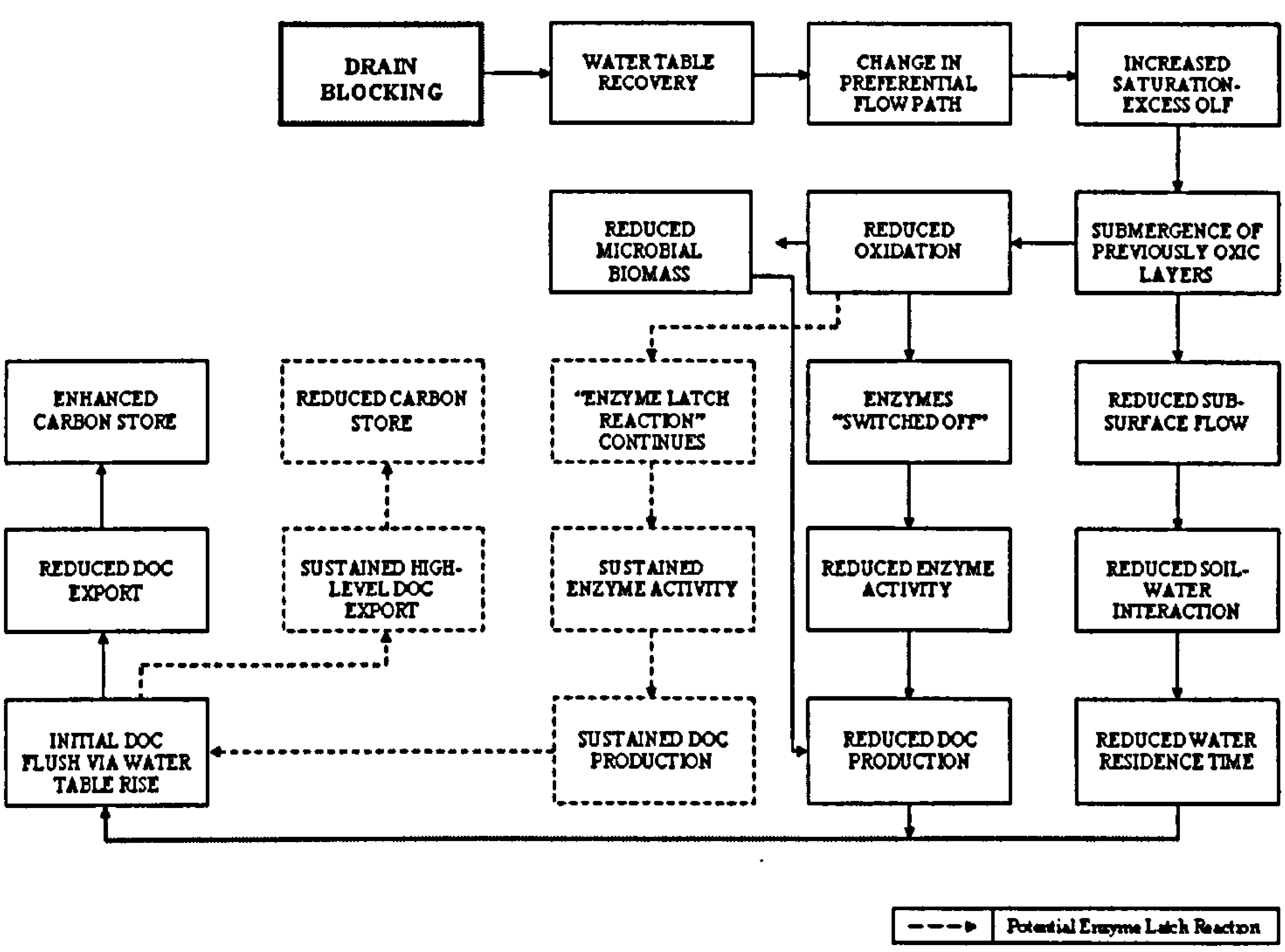


Figure 2.6 A summarised conceptual model of the processes likely to be affected by drain blocking.

2.10. SUMMARY AND CONCLUSIONS

Enhanced levels of DOC and water discolouration are often observed in drained blanket peat catchments (e.g. Clausen 1980; Edwards 1987; Mitchell & McDonald 1992a; 1995; Worrall *et al.* 2003). However, to date such research has generally only been concerned with monitoring water quality issues rather than trying to unravel the intimate processes likely to responsible. It appears enhanced DOC and colour values may be the result of a prolonged period of water table drawdown increasing the level of oxygenation within the peat body. Increased oxygenation has been shown to stimulate the activity of phenol oxidase enzymes resulting in the subsequent removal of inhibitory phenolic compounds, which allows for enhanced peat decomposition by pivotal hydrolase enzymes and thus greater DOC production (Freeman *et al.* 2001b). In addition, the dominance of water flowpaths in peat varies depending on water table depth in conjunction with antecedent conditions and topographic position (Wallage *et al.* 2006). Therefore, water table disturbance may also alter the hydrological routing of water through and across the peat, such that alternative sources of DOC are made accessible.

In response to such a threat to carbon storage potential and water quality, a significant amount of work toward ecological restoration has taken place, although a great deal of this work has been carried out on a pragmatic or even an ad-hoc basis, which reflects both the urgency of the requirement to protect important sites, and the frequent shortfalls in available funding. Consequently, the effects of peatland restoration on DOC and colour dynamics are very poorly understood, with only a few studies undertaken in this area and with contradictory results already prominent (e.g. Glatzel *et al.* 2003; Wallage *et al.* 2006; Worrall *et al.* 2007a). It would seem that the rewetting associated with drain blocking may not necessarily be successful in reducing DOC and water discolouration. For example, Freeman *et al.* (2001b) suggested that the loss of phenolic compounds caused by the oxygenation associated with water table drawdown means that it is possible for decomposition to continue at depth even after the water table has been restored. A process that has been referred to as the 'enzyme latch' mechanism; enzymes are 'switched on' by water table drawdown but are then not 'switched off' as the water table recovers. In addition, water table disturbance in the form of drain blocking could also alter the hydrological routing of water through and across the peat, altering the accessibility of potential DOC sources due to changes in the hydrophysical peat properties modifying the contact time and the area between the solid and liquid phase, which could be an important control on DOC release.

The full effects of drainage and drain blocking on DOC and colour dynamics are difficult to assess and are likely to be extremely complex. A reduction or loss of natural carbon sinks and the creation of CO_2 sources represents a significant problem from the standpoint of global climate change, and it is therefore imperative that we improve our understanding of how blanket peat and the fluvial carbon flux responds to water table modification. An intensive, process-based approach is required in order to identify which mechanisms are involved, be they chemical, physical, hydrological and biological, and how they interact. The results will have potentially national and global applications with respect to improving carbon storage potential and ameliorating water discolouration. Improving our knowledge of the processes involved is extremely important given that although the analogy with the effects of climate change is undoubtedly not complete, drained peat probably shows, to a certain extent, what would happen if large scale drying were to occur.

CHAPTER 3

STUDY SITE AND SAMPLING REGIME

3.1. SELECTION OF STUDY SITE

This thesis is concerned with establishing the effects of installing artificial drainage ditches in blanket peat soils on the key mechanisms that influence DOC and colour dynamics in such environments; and the efficiency to which drain blocking is able to restore DOC and colour levels relative to those currently observed in undisturbed blanket peat. Such a process-based assessment required an intensive plot-scale investigation and sampling regime that incorporated a range of field monitoring and laboratory measurements. Therefore, it was of practical importance to choose a study site that was easily accessible, permitted consecutive day sampling and was located in a typical area of upland blanket peat moorland, where permission for land access and instrumentation could be gained. The field site that satisfied this criteria was the Oughtershaw Beck catchment, which is situated 50 miles northwest of Leeds in the heart of the Yorkshire Dales National Park, northern England (Figure 3.1). The moorland areas of this region are extensive and internationally important for their populations of breeding birds, including merlin and golden plover, and are generally defined by three broad habitats; dry heath, bog and acidic grassland (Thom & Court 2000). These bogs are generally associated with relatively deep peat formations virtually all of which occur as blanket peat, such as those found at Oughtershaw that range in depth from 0.5 to 2.5 m (Holden 2006). Blanket peat soils cover approximately 7.5 % of Britain and represent the largest single global contribution of blanket peat (10-15 %), whilst the blanket peat located in the Pennines region, where the high humidity in association the underlying impervious glacial till allow the spread of the mire over sloping terrain, represents one of the largest distributions located in Britain (Tallis 1998; Charman 2002). Added incentive to the site selection was the recent (September 1998) establishment of meteorological and hydrological monitoring stations by the Environment Agency to the catchment (Dunn 2000).

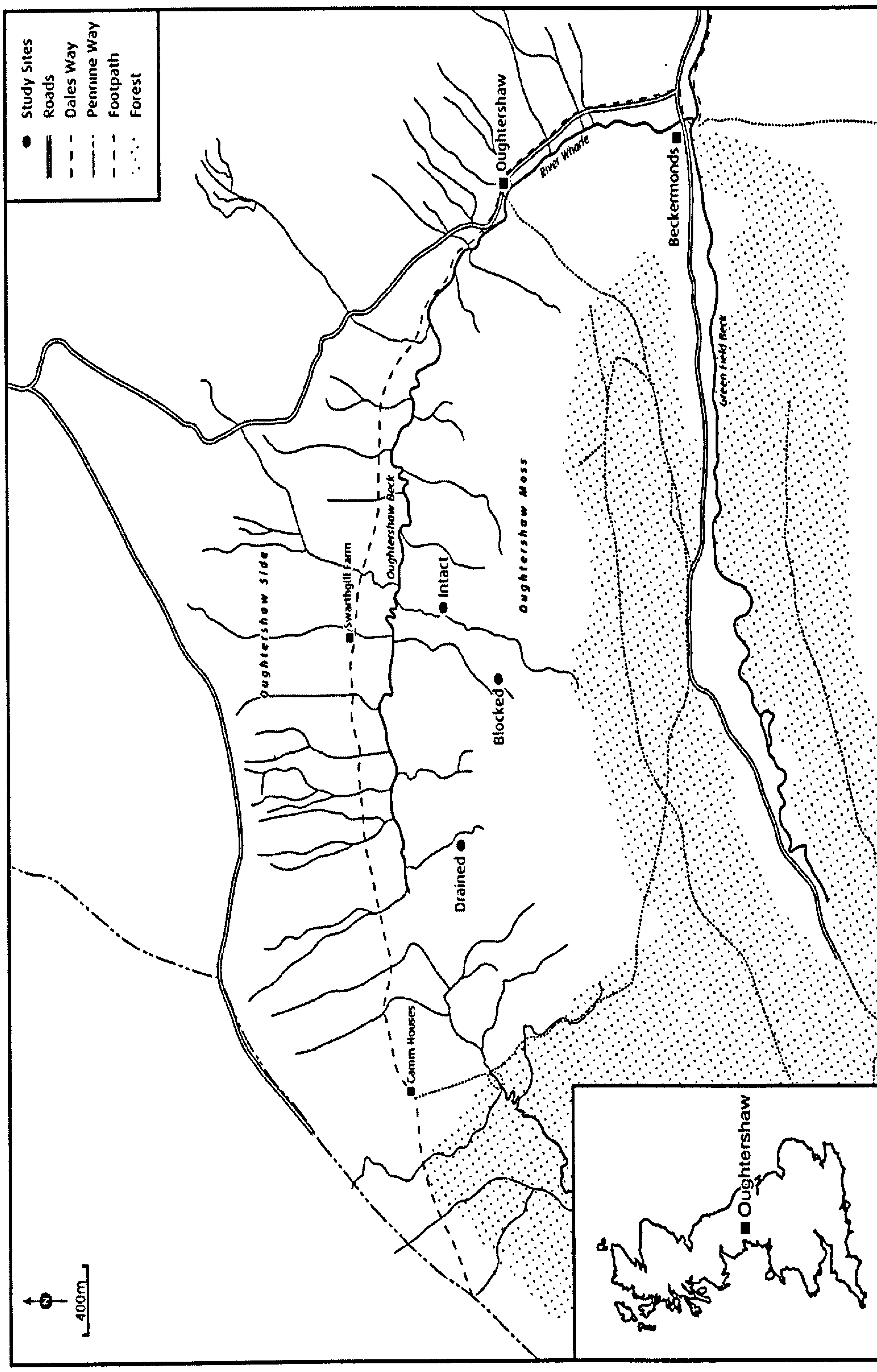


Figure 3.1 The location of Oughtershaw Beck and the three study sites (Intact, Drained and Blocked).

3.2. SITE DESCRIPTION

Oughtershaw Beck (54°14' N; 2°14' W) is a headwater tributary of the River Wharfe; a river which for most of its 97 km length provides the county boundary between West and North Yorkshire, before its confluence with the River Ouse near Cawood, Selby. Figure 3.2 shows an overview of the small 13.8 km^2 upland catchment of Oughtershaw Beck, which experiences an oceanic climate that is dominated by 1800 mm of precipitation per year and a mean annual temperature of 6°C (Holden 2006). The catchment is underlain by Carboniferous limestone and Millstone Grit that is covered with a glacial boulder clay deposit, which in conjunction with the high annual rainfall and deforestation around 7,000 years ago, has resulted in the development of an acidic Winter Hill blanket peat deposit (Avery 1980; Urquhart 1987).

The Soil Survey classification describes the Winter Hill association as very acidic, oligo-fibrous blanket peat that occurs to a minimum depth of 40 cm, making it the deepest organic soil in the classification (Avery 1980). Winter Hill peat is the main blanket bog soil type in England and Wales and covers an area of 2575 km^2 (Garnett *et al.* 2001). Mitchell and McDonald (1995) identified that this soil type represents one of the primary sources of DOC and discoloured water to upland waters in North Yorkshire. The blanket peat at Oughtershaw occurs on slopes up to 15° and the dominant vegetation is *Eriophorum* sp. with some *Sphagnum* cover (Holden 2006). The average soil pH is 3.4, and in un-drained areas of peat the water table resides within 10 cm of the surface for 75 % of the time (Boswell 1955; Holden 2006). Only during short periods during the summer months does the water table decline to levels below this, with a maximum water table depth of 25 cm recorded during the period December 2002 to December 2004 (Holden 2006).

During the 1960s, a large proportion of the Oughtershaw catchment was artificially drained via the installation of open-cut ditches to the soil, which were dug to a depth of approximately 50 cm (Figure 3.3). Most of the ditches are spaced at between 45 and 50 m, although in some areas of the catchment this has been found to be reduced to 20 m. A sample of the drain networks were blocked with peat dams in 1999 and by

Figure 3.2 The Oughtershaw Beck catchment, looking north-west towards Camm Houses.

Figure 3.3 The Oughtershaw Beck catchment looking north-east. Several drainage ditches can be seen running across the slope, terminating near the gully.

Figure 3.4 A close-up view of a blocked ditch. Ponding can be seen behind the dam and new *Sphagnum* growth directly under the water.

Figure 3.5 A close-up view of one of the open ditches sampled. Although difficult to see, a network of piezometers at 5, 10, 20, and 40 cm depths, a crest-stage tube for OLF and a dip-well are located on either side of the ditch.

2000 approximately 30 km had been blocked using peat dams with the help of the North Yorkshire Farming and Wildlife Advisory Group and the Environment Agency. Blocking involved cutting a section of peat ~1 m^3 from the upslope side of the ditch and using this to create a peat dam at regular intervals along the course of the drain. As seen in Figure 3.4, blocking helps slow down the transfer of water through the ditch by allowing it to pond behind the dam, which encourages sediment accumulation and vegetation colonisation. During flow events, water may overspill from the pond, which generates OLF that helps to rewet the peat surface.

3.3. SAMPLING REGIME

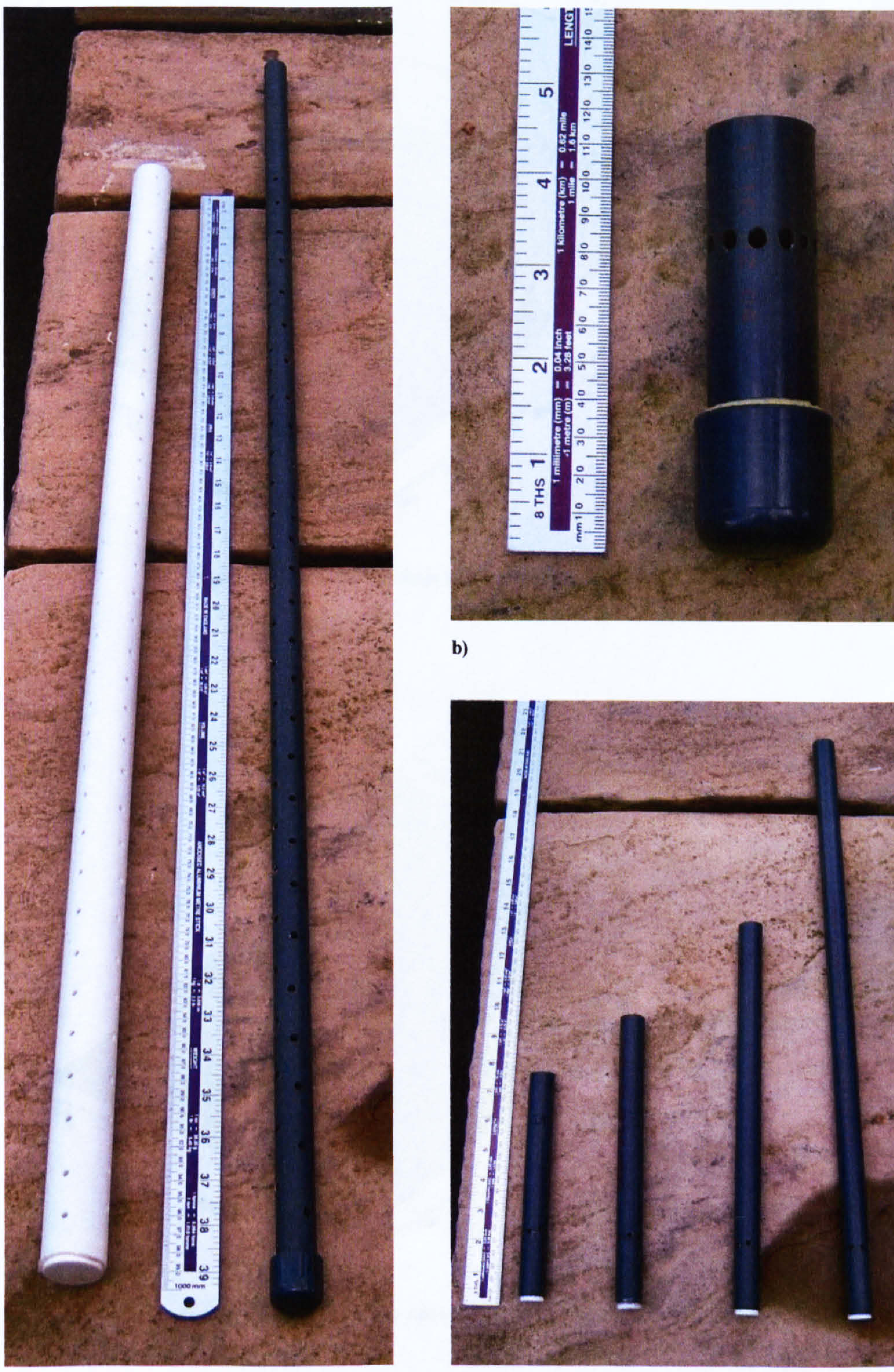
In order to predict the consequences and extent of environmental change on blanket peat, whether the change is direct such as drainage or restoration or inadvertent such as climate change, it is imperative that processes are monitored on an intensive scale in order to identify the key mechanisms influencing DOC and colour dynamics. Two hillslopes that were typical of the drained and drain-blocked land management techniques carried out in the catchment were randomly chosen for the two treatment sites, whilst an un-drained "intact" hillslope was selected for the control site. As data were to be compared between these three hillslopes, it was vital to keep as many of the site characteristics as similar as possible. Therefore, the sites were located within 1.2 km or less of each other and on slopes with comparable angle, aspect and drainage area. Although there was a slight (< 35 m) variation in altitude between two of the sites, a habitat and vegetation survey undertaken by the Environment Agency at Oughtershaw in June 2002 identified no obvious differences in vegetation between sites located at the top of a slope and those located nearer the base, with both areas consisting of light to moderately grazed blanket bog dominated by graminoid species (Mastel 2002) (Appendices 1 & 2). The report also provided results of a vegetation survey that was undertaken in an attempt to acquire baseline data relating to the effects of drainage and restoration on species diversity (Appendices 3 & 4), and concluded there were no obvious differences in diversity between a drained site and a site where the drains had recently been blocked, which, coincidently, were located similar distances apart to those used in this study.

Although there is likely to still be some variation between the three sites, the level of unsystematic error was kept to a minimum by installing identical sampling strategies on each hillslope. This involved the installation of two 60 m transects that ran vertically down each hillslope, and which each contained fourteen individual sample-point stations; resulting in a total of twenty-eight being located at each site. As seen in Figure 3.5, each sample-point station was instrumented with a crest-stage tube to monitor the occurrence of overland flow; four piezometers (at depths of 5, 10, 20 and 40 cm) to collect soil water solutions, and one dip-well to measure the depth of the water table. The six tubes at each sample-point were spaced evenly apart at a distance of ~30 cm (Figure 3.6). All the tubes were made from PVC, but consisted of two differently sized external diameters; 2.5 cm, which was used for the piezometers and manually measured dip-wells, and 4 cm, which was used for the crest-stage tubes and for the dip-wells that would be automated with pressure transducers. All tubes were sealed at the base, whilst the exposed top 5-10 cm had a plastic cap inserted to protect the soil water samples from dilution and contamination (Figure 3.7).

Figure 3.6 A close-up view of some of the piezometers that were installed at Oughtershaw, detailing the spacing between instruments and the typical vegetation found within the catchment.

The crest-stage tubes were 10 cm in length and had flow entry points positioned into the tube at 5 cm, which allowed the tubes to fill with water whenever there was any surface water flowing over the peat surface. Dip-wells totalled 1.1 m in length and had holes drilled the length of the tube to allow water to enter from the entire depth of the soil that was sampled, which allowed an open level of water to develop that was hydraulically connected with the groundwater (Gilman 1994). The piezometers only had holes drilled at the depth at which soil waters were to be investigated (5, 10, 20 and 40 cm) and the tubes varied in length from 20 cm to 55 cm as each had a 5 cm reservoir area to store soil water and an extra 10 cm that was exposed above the soil surface. The distance between the sample-point stations located across each transect varied. 1 m spacing was used between the first five stations positioned up-slope of the drain/block and the first three stations down-slope; whilst 10 m spacing was used between the remaining six stations located further up/down-slope. The close spacing of instruments around the drains allowed high resolution data to be collected around the areas thought to be of greatest influence to DOC and colour. The sample design was repeated at the intact site to ensure the data was not influenced by the sampling regime, with the individual set-up for each hillslope shown in Figures 3.8 to 3.10.

Soil water monitoring and sample extraction was carried out at monthly intervals during January 2005 to November 2005. However, at the drained site it was not possible to collect samples during September and October as access to the site was restricted due to the yearly grouse shooting season; whilst no samples were able to be collected from the blocked site in January due to equipment failure. Soil water samples were extracted from the piezometers and crest-stage tubes using lengths of Tygon R3603 tubing attached to 20 ml Plastipak syringes. The syringes had 25 mm syringe filter holders attached that housed Whatman WCN 0.45 μm filter papers, which allowed a large number of samples to be filtered relatively easily and quickly in the field (Figures 3.11 and 3.12). Immediately after filtration, the samples were transferred to 20 ml plastic screw-cap containers and stored in the dark at 4°C within 12 hours of collection (Figure 3.13). Full details of the water sampling protocols undertaken in this thesis can be found in Sykes and Lane (1996), whilst the chemical methods of analysis are presented in Section 4.2.



b)

a) c)

Figure 3.7 Monitoring devices for examining flow processes: a) Dip-wells, 2.5 cm and 4 cm in external diameter (E.D.); b) Crest-stage tube, 4 cm (E.D.); c) Piezometers, 2.5 cm (E.D.).

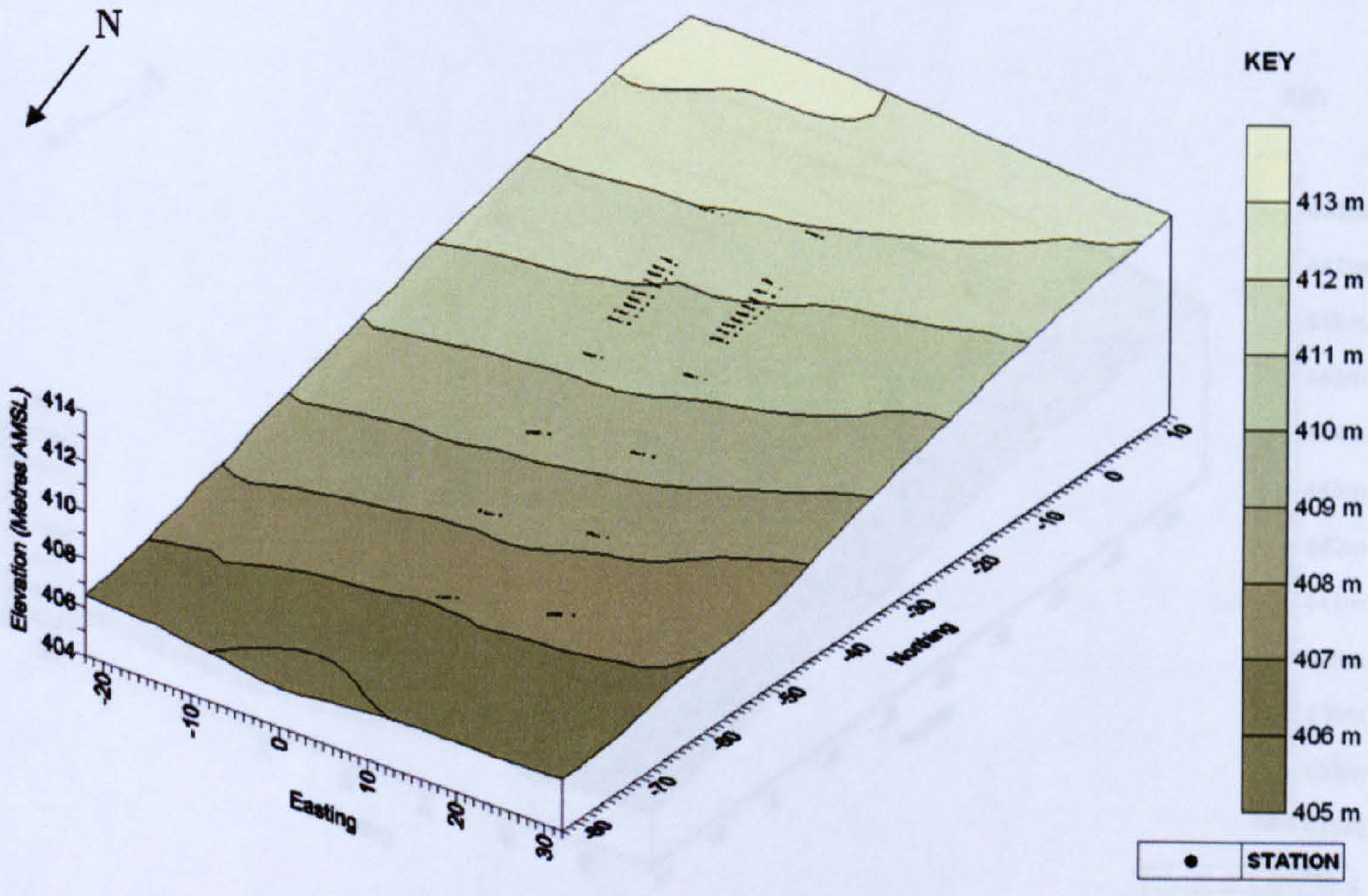


Figure 3.8 The intact site slope profile and sample station position.

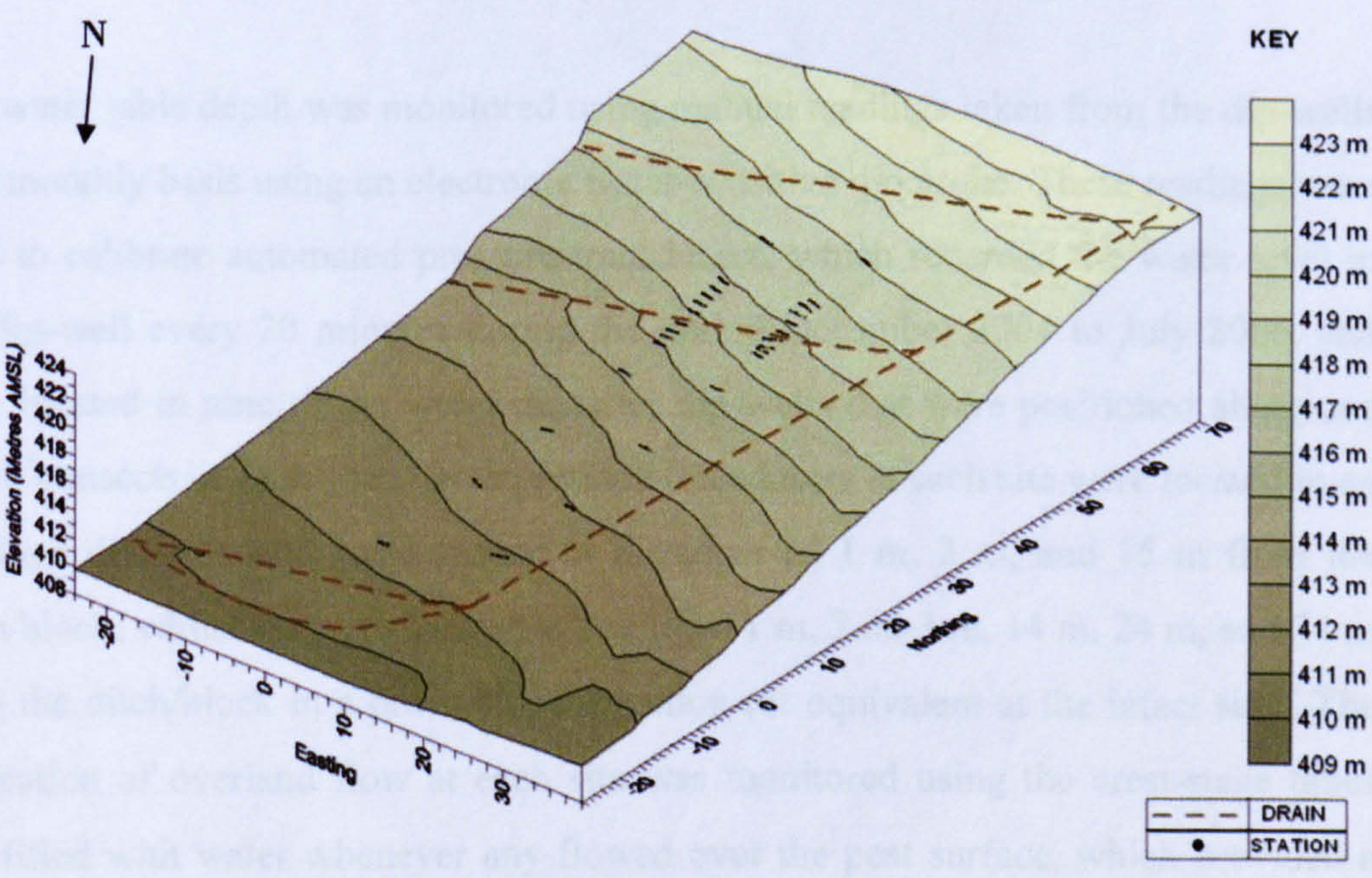


Figure 3.9 The drained site slope profile and sample station position.

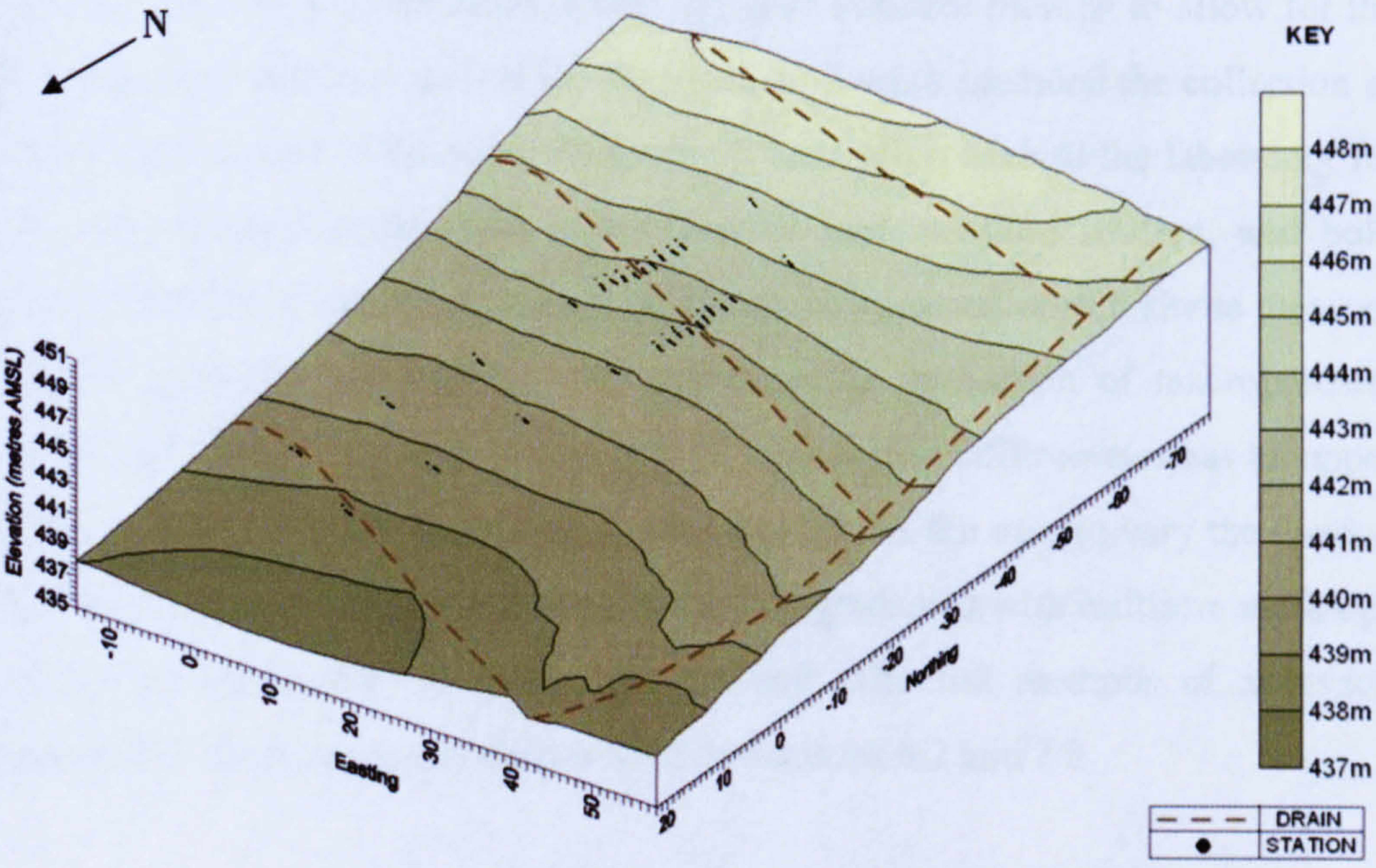


Figure 3.10 The blocked site slope profile and sample station position.

The water table depth was monitored using manual readings taken from the dip-wells on a monthly basis using an electronic water-sensitive dip probe. These readings were used to calibrate automated pressure transducers, which recorded the water level in the dip-well every 20 minutes during the period December 2004 to July 2006, and were located in nine of the wider diameter dip-wells that were positioned along one of the transects at each site. Three pressure transducers at each site were located in an up-slope direction and were spaced at distances of 1 m, 2 m, and 15 m from the ditch/block; whilst six were located at positions 1 m, 2 m, 3 m, 14 m, 24 m, and 34 m from the ditch/block in a down-slope direction (or equivalent at the intact site). The generation of overland flow at each site was monitored using the crest-stage tubes that filled with water whenever any flowed over the peat surface, which provided a means of monitoring the occurrence of overland flow between sampling intervals when the tubes were emptied for soil water analysis. Full methods of hydrological analysis are presented in Section 7.2.

Additional monitoring and experimental programmes were carried out at each site to measure and compare the biological and physical processes operating under each land management, and were undertaken during the drier summer months to allow for the biggest difference between sites to be observed. This work included the collection of soil samples from each of the three sites, which were taken back to the laboratory for analysis of enzyme activity, soil organic matter and moisture content, and bulk density. In addition, a mini-disk tension infiltrometer was used at each site to measure the rate of hydraulic conductivity and determine the proportion of macroporosity within the soil surface. As seen in Figure 3.14, the tension infiltrometer has an upper (bubble) chamber with a suction control tube that allows the user to vary the tension at which water is held; and a lower chamber that is graduated with millilitre markings and holds the water that infiltrates into the soil. The full methods of approach undertaken for these processes are provided in Sections 6.2 and 7.2.

Figure 3.11 The in-field sampling and filtering strategy, with soil waters being extracted into syringes with 0.45μm filters attached.

Figure 3.12 A close-up view of the sampling and filtering strategy for soil water solutions at Oughtershaw.

Figure 3.13 The collection and storage of filtered soil water samples.

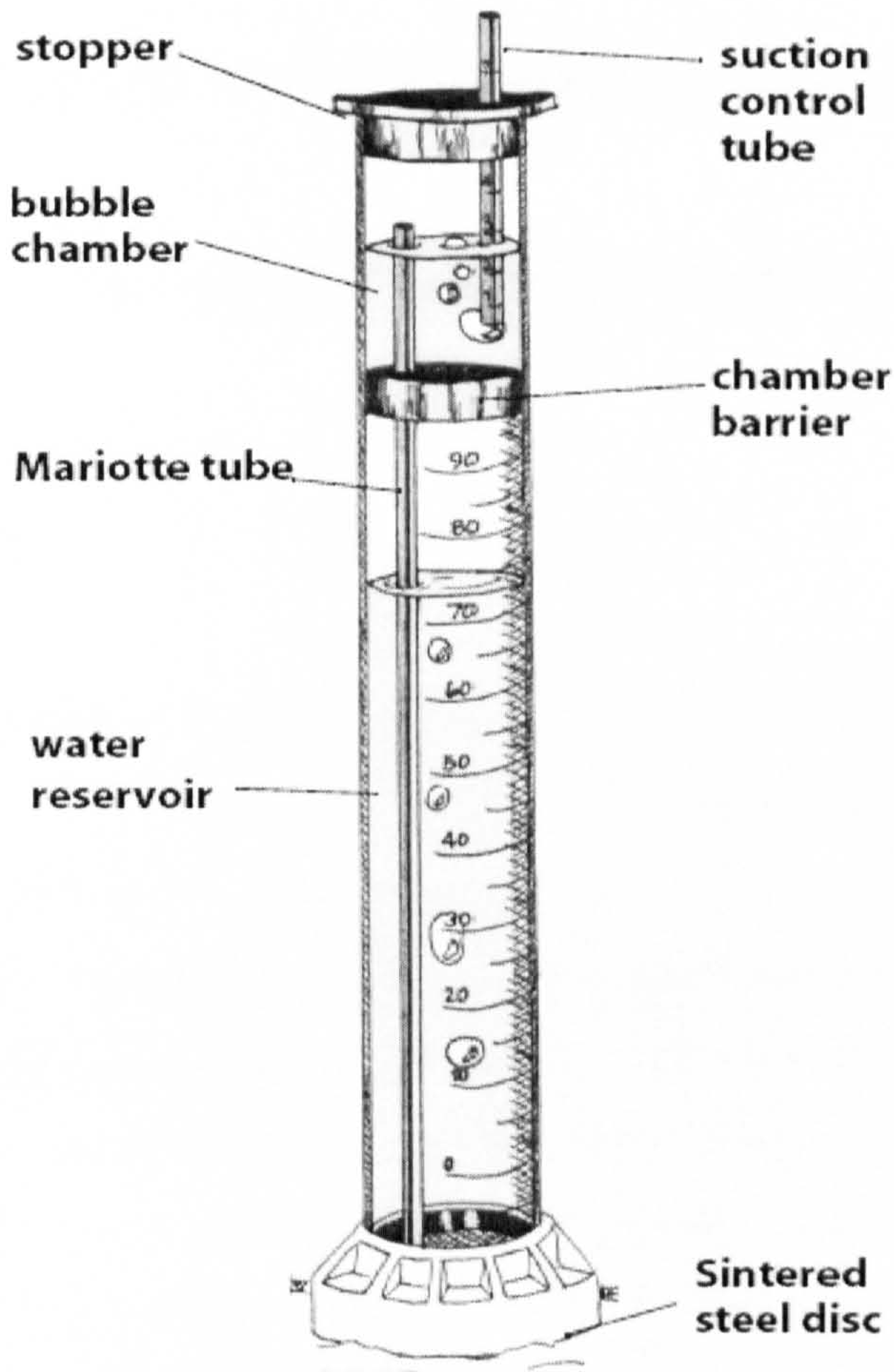


Figure 3.14 Diagrammatic of a mini-disk tension infiltrometer, sourced from Decagon (2005).

CHAPTER 4

DOC RELEASE AND WATER DISCOLOURATION IN DRAINED AND RESTORED BLANKET PEAT

4.1. INTRODUCTION

Elevated DOC concentrations and an associated rise in water discolouration are often observed in drained blanket peat catchments (e.g. Clausen 1980; Edwards 1987; Mitchell & McDonald 1992a; 1995; Worrall *et al.* 2003). Consequently, in recent years there has been a significant amount of work towards peatland restoration, in the form of drain blocking, in an attempt to improve both the carbon storage potential and water quality of these sensitive upland ecosystems. However, the majority of this work has been carried out on a pragmatic or even an ad-hoc basis, which reflects both the urgency of the requirement to protect these important sites, and the frequent shortfalls in available funding (Holden *et al.* 2006). Thus, the effect of drain blocking on DOC and colour dynamics in blanket peat soils is very poorly understood with only a few studies undertaken, and which have already provided contradictory results (e.g. Glatzel *et al.* 2003; Wallage *et al.* 2006; Worrall *et al.* 2007a).

The aim of Chapter 4 therefore is to provide an in-depth assessment of the variability in DOC and water colour dynamics in soil-water solutions extracted from drained and drain-blocked blanket peat, in order to determine how they compare to an area of undisturbed blanket peat, as set out in Objectives 1 and 2 of Section 1.2. Chapter 4 is thus fundamental to the thesis in that it i) establishes the principal differences in DOC concentrations and water colour levels, and thus the likely carbon storage potential and water quality, between intact and drained blanket peat; ii) determines whether peatland restoration in the form of drain blocking is a successful technique for reducing the release of DOC and discoloured waters, and thus reverting the ecosystem back to a net carbon sink and ameliorating water quality; and iii) is a prerequisite for identifying the likely processes responsible for alterations to DOC and colour dynamics between the three land managements, which are then further explored in Chapters 6 and 7.

In addition, any changes to the composition and therefore character of the DOC released will ultimately affect the proportion of labile to refractory DOC, which could alter the level of reactivity of DOC and therefore its THM formation potential. Not only could this influence the way that DOC is transferred through the global carbon cycle, but also the ability to which DOC and colour can be removed at the potable water treatment works. Therefore, Chapter 4 also provides a qualitative assessment of DOC composition using spectrophotometric techniques to determine both the humic – fulvic (E4/E6) ratio and colour – carbon (C/C) ratio, in order to discriminate between basic DOC fractions and thus identify the likely treatability of runoff produced from each of the three land managements.

4.2. METHODS

Over the period January to November 2005, a total of 1,382 soil water solution samples were extracted from the three sites. Samples were collected at monthly intervals from the piezometers and crest-stage tubes located at the sample-point stations situated along one of the transects located on each site. The piezometers were used to sample porewaters at depths of 5, 10, 20 and 40 cm, whilst the crest-stage tubes were used to sample overland flow at the soil surface (0 cm). Samples were extracted using lengths of Tygon R3603 tubing attached to 20 ml Plastipak syringes, which had 25 mm syringe filter holders housing Whatman WCN 0.45 µm filter papers. Once filtered, the samples were transferred to 20 ml plastic screw-cap containers and stored in the dark at 4°C within 12 hours of collection. Full details of the water sampling protocols used can be found in Sykes and Lane (1996).

DOC concentration was measured using a Thermalox Total Carbon (TC) analyser, which has a precision of ± 0.1 mg C l^{-1} and a minimum detection limit of 1 mg C l^{-1}. Prior to analysis, samples were acidified and sparged with oxygen to stabilise the sample and to remove any inorganic carbon. Then, the acidified samples were run through the TC analyser in duplicate (or triplicate if the coefficient of variation [CV] >1 %), with the DOC concentration determined by a seven-point calibration curve created using the standard DOC calibration compound, potassium hydrogen phthalate (KHP). In addition, regular analysis of KHP standards and a certified reference material (VKI QC WW4a) ensured that the level of error was kept to a minimum. Water colour was measured using a HACH DR/2010 spectrophotometer set at wavelengths of 400, 436, 465, and 665 nm, which has a precision of ±0.002 abs. To take account of the variability in cell path lengths between spectrophotometric instruments, absorbance readings (abs) were converted to standardised water colour measurements of absorbance units per metre (au m^{-1}) by multiplying the liquid cell width by the appropriate factor (Mitchell & McDonald 1992b).

To understand how changes in land management affect DOC and colour dynamics, it is also important to determine the sources and general composition of DOC/colour. In order to differentiate between microbial and plant/soil precursor materials the colour – carbon (C/C) ratio was used, which is also known as the specific UV absorbance (SUVA). The C/C ratio was obtained by dividing the absorbance values at 400 nm (Abs^{400}) by the corresponding DOC concentrations. In prior research, SUVA has been used at many wavelengths (e.g. 254, 280, 400), but its general principle of use stays the same; aromatic groups, which are more abundant in humic substances have a higher C/C ratio (higher SUVA) and are derived from more lignaceous materials and thus tend to absorb UV radiation more strongly than aliphatic groups (Mladenov *et al.* 2005).

In addition, within a relatively homogeneous soil profile the variability in the C/C ratio can be used as a relative indication of the level of microbial activity. This is because within internal cycling of the peat soil organisms, principally fungi and bacteria, metabolise the non-coloured, small molecular mass non-humic compounds in preference to the larger, more biologically resistant coloured humic substances (Dawson *et al.* 2001; Hope *et al.* 1994; Thurman 1985). Consequently, a high C/C ratio indicates that the DOC comprises a greater proportion of coloured humic substances compared to uncoloured non-humic substances, which could be used to imply a heightened level of microbial activity in the peat than that where a sample exhibits a lower C/C ratio. In order to provide further evidence as to whether any compositional changes had occurred, the E4/E6 ratio was determined for each sample, which measures the proportion of fulvic acid to humic acid in the coloured humic component of DOC. The E4/E6 ratio was calculated by dividing the absorbance at 465 nm (Abs^{465}) by that at 665 nm (Abs^{665}) for the individual samples.

As a complete dataset using values from all three treatments, the DOC data was found to be positively skewed (Figure 4.1). Therefore, a log transformation was used in order to normalise the data. The water colour data (at 400, 436, 465 and 665nm) and the associated E4/E6 ratio were also found to be positively skewed (e.g. Figures 4.2 & 4.3); however, these responded better to a square root transformation. In contrast, the C/C ratio was found to be normally distributed, so did not require any transformation (Figure 4.4). Data were also checked for homogeneity (equality) of variances using the Levene's test before parametric tests of differences were applied, which included analysis of variance (ANOVA) (or the Welch *F* ANOVA method if unequal variance was identified) and the independent Student's t-test. Tests of difference in DOC concentration, water colour and the C/C and E4/E6 ratios were initially performed between the three sites to give an overview as to how changes in land management (i.e. drainage and drain blocking) may affect these variables. Subsequently, it was necessary to see if any of the differences identified between the sites varied on a temporal basis, and this was done by comparing mean monthly values obtained throughout the sample period (January – November 2005). Finally, in order to help identify the processes involved, and thus try and provide an answer to the question of why there may be differences between sites, it was necessary to assess how these factors varied on a spatial scale within each site; this was done by using ANOVA to identify differences in DOC, water colour, C/C and E4/E6 ratio between soil depths at each of the sites and by constructing transect plots to try and identify the key areas of influence along each of the three hillslopes.

4.3. RESULTS

4.3.1. DOC AND COLOUR VARIABILITY BETWEEN SITES

ANOVA identified there to be significant (p <0.001) differences in mean DOC concentrations and water colour values between all three sites (Figure 4.5, Table 4.1). For DOC, values from the drained peat were significantly higher than those for the intact peat, which in turn were significantly greater than those from the blocked site. For colour (absorbance at 400nm) there were significant (p <0.001) differences between the intact and drained sites, and drained and blocked sites, but no significant (p = 0.116) difference was identified between the intact and blocked sites (Figure 4.6, Table 4.1). A similar pattern was evident in water colour measured at the higher wavelength of 436nm, although the differences between sites were less significant. When the wavelengths of 400nm and 436nm were compared, it was found that the level of absorbance decreased with increasing wavelength, indicating that colour measurements at 400nm incur a higher level of precision than at 436m and thus analysis at 400nm is more sensitive for determining variations in water colour between sites. In addition, most UK water companies measure colour at 400nm in order to comply with the EC maximum colour standard for treated water of 1.5 au m^{-1}, which is set at 400nm (Reynolds *et al.* 1995). Therefore, all further analysis of water colour is reported for absorbance at 400nm.

Although there was a significant (p <0.001) and strongly positive (0.88) correlation between DOC and Abs^{400}, ANOVA identified there to be significant (p <0.001) differences in the C/C ratio between sites (Figure 4.7). In addition, independent t-tests showed that the mean C/C ratios for the intact and drained sites were not significantly different, but both were significantly (p <0.001) lower than that of the blocked site (Table 4.1). This means that for a sample with a DOC concentration of 100 mg C l^{-1}, the Abs^{400} from the intact and drained peat would be approximately 48.0 au m^{-1}, whereas the Abs^{400} from the blocked site would be higher at 55.0 au m^{-1}. The higher C/C ratio at the blocked site highlights the fact that although this treatment has the lowest DOC and Abs^{400} values, per carbon unit, the DOC actually contains more colour than the two other sites. Mean E4/E6 ratios were also found to differ significantly between the three treatments at p <0.001, and independent t-tests identified that although the mean E4/E6 ratio for the drained and blocked sites was not significantly different (p 0.804), both were significantly ($p < 0.001$) lower than the intact site (Figure 4.8, Table 4.1). The higher E4/E6 ratio at the intact site indicates that the action of drainage and drain blocking appears to have modified not only the concentration of DOC but also the composition, with the DOC in the intact site samples appearing to be dominated by more fulvic material.

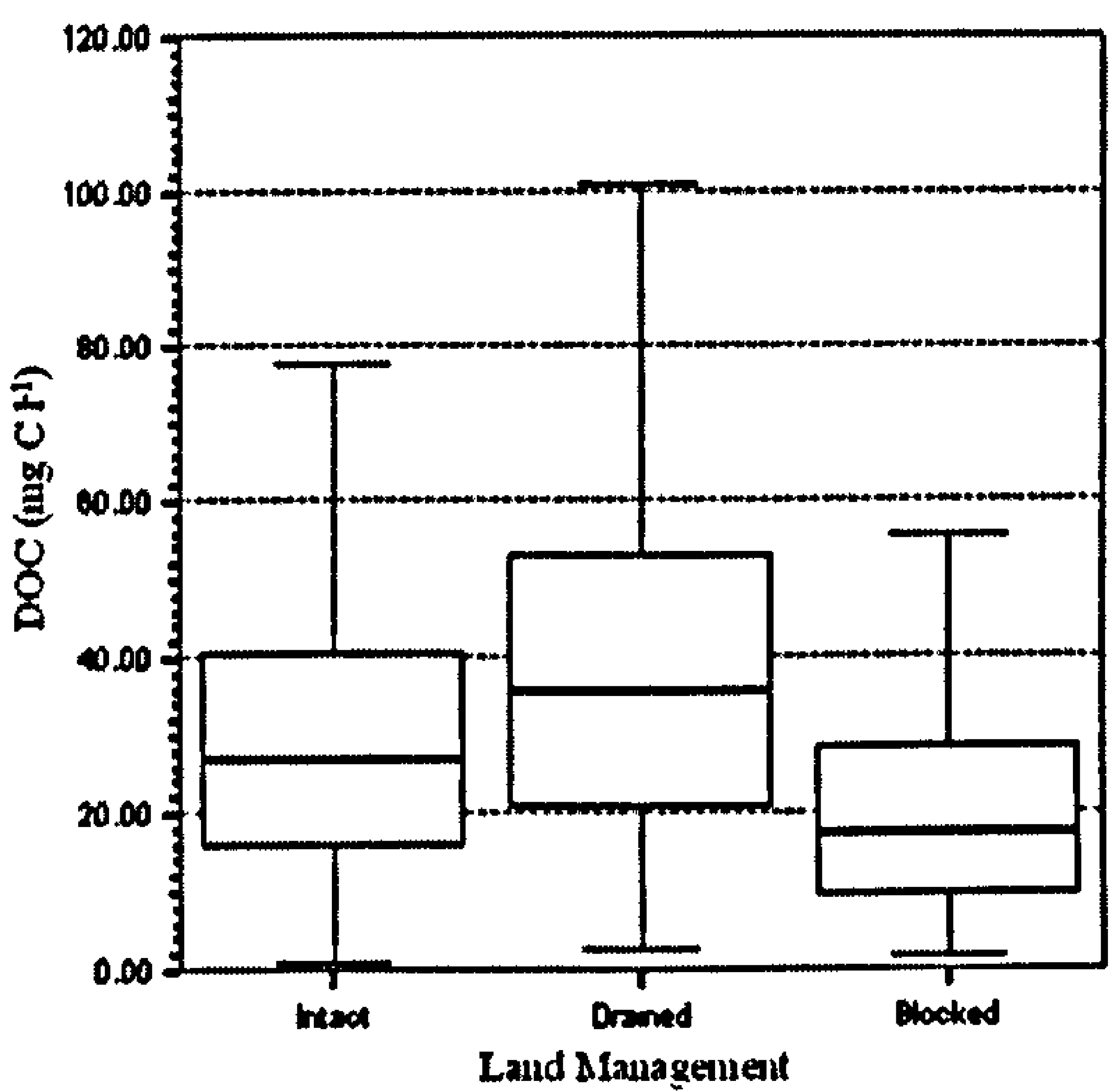


Figure 4.1 A box-plot identifying the spread of the untransformed DOC data for the three treatments.

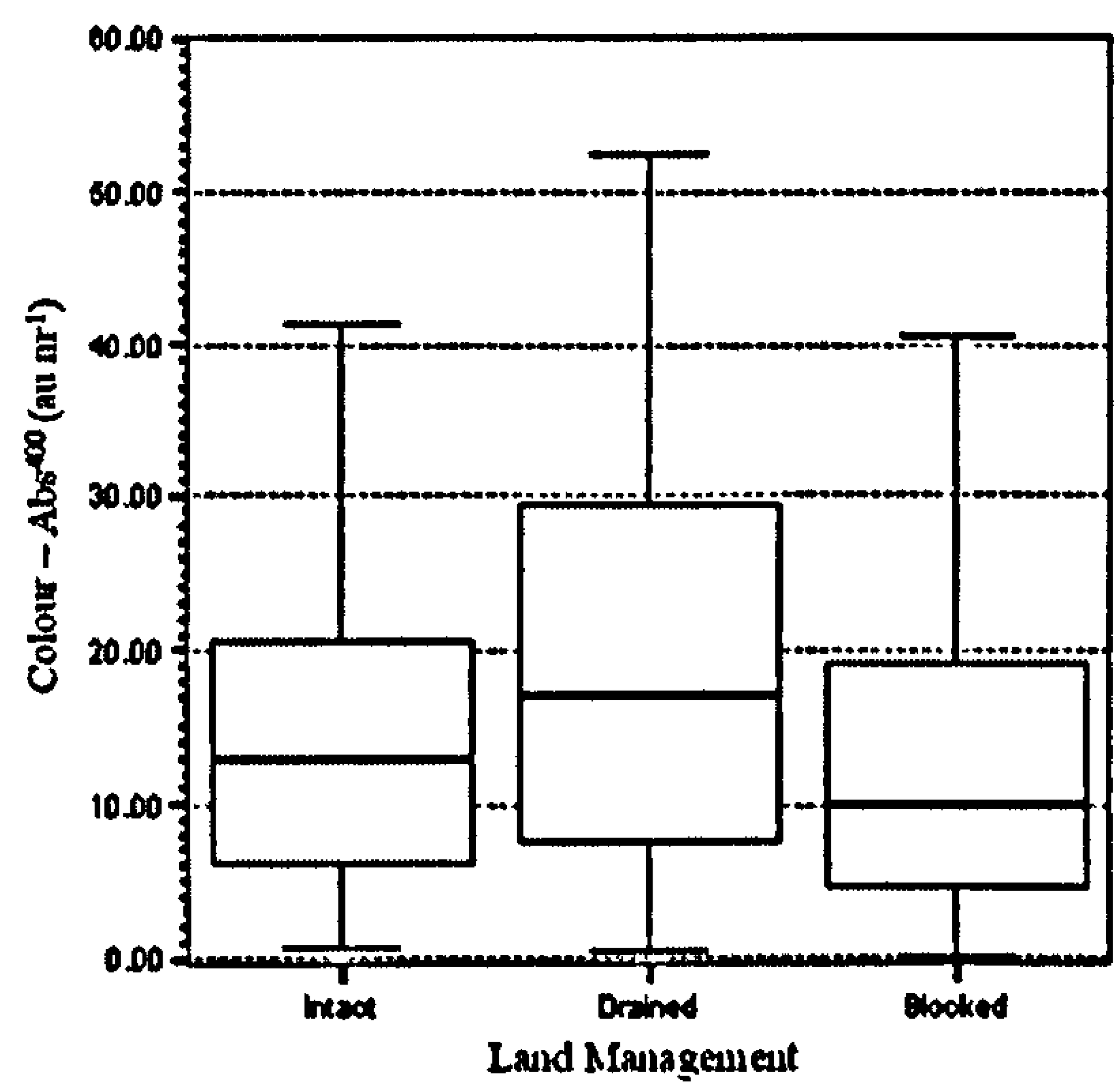


Figure 4.2 A box-plot identifying the spread of the untransformed colour (Abs^{400}) data for the three treatments.

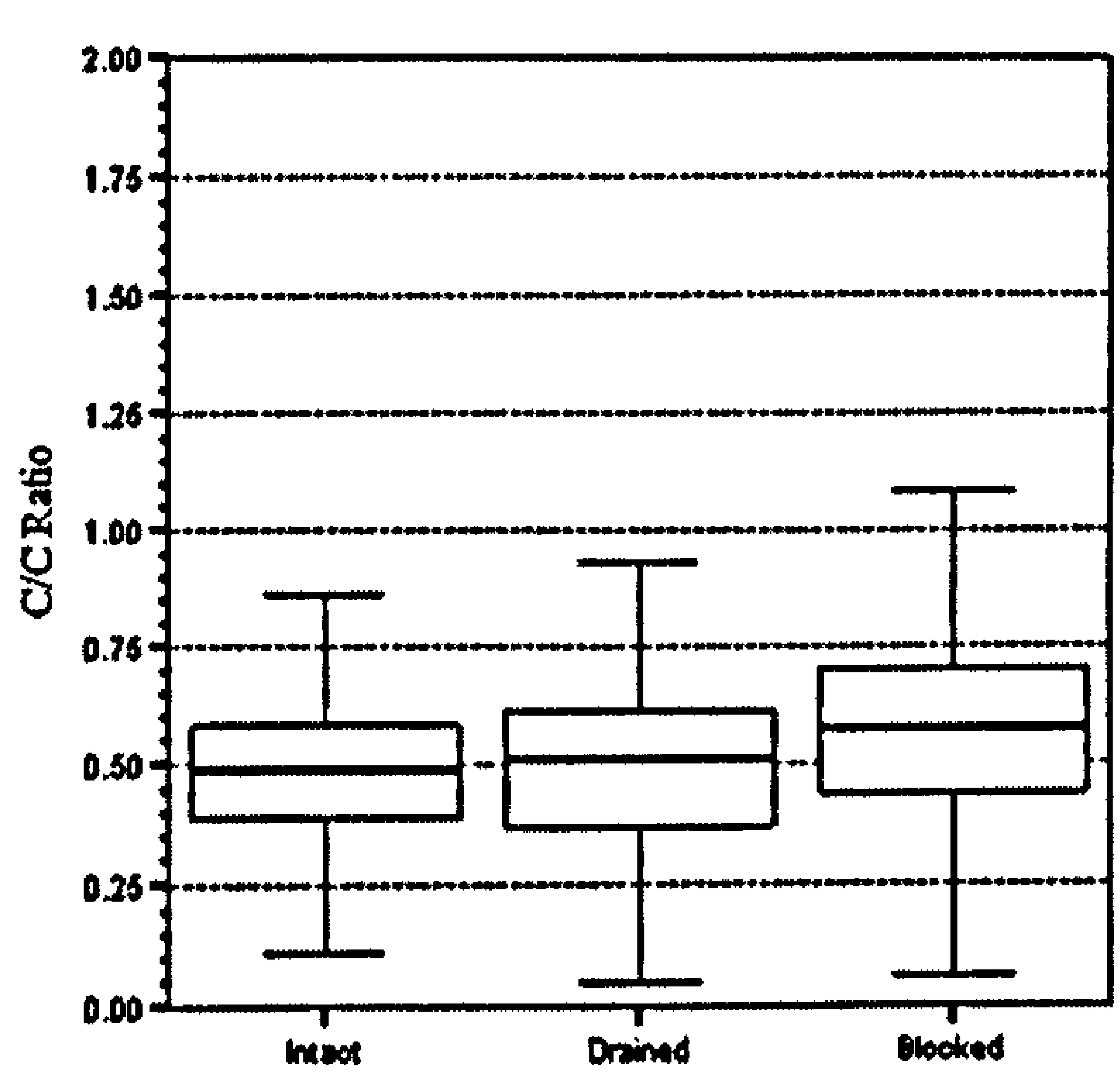


Figure 4.3 A box-plot identifying the spread of the C/C ratio data for the three treatments.

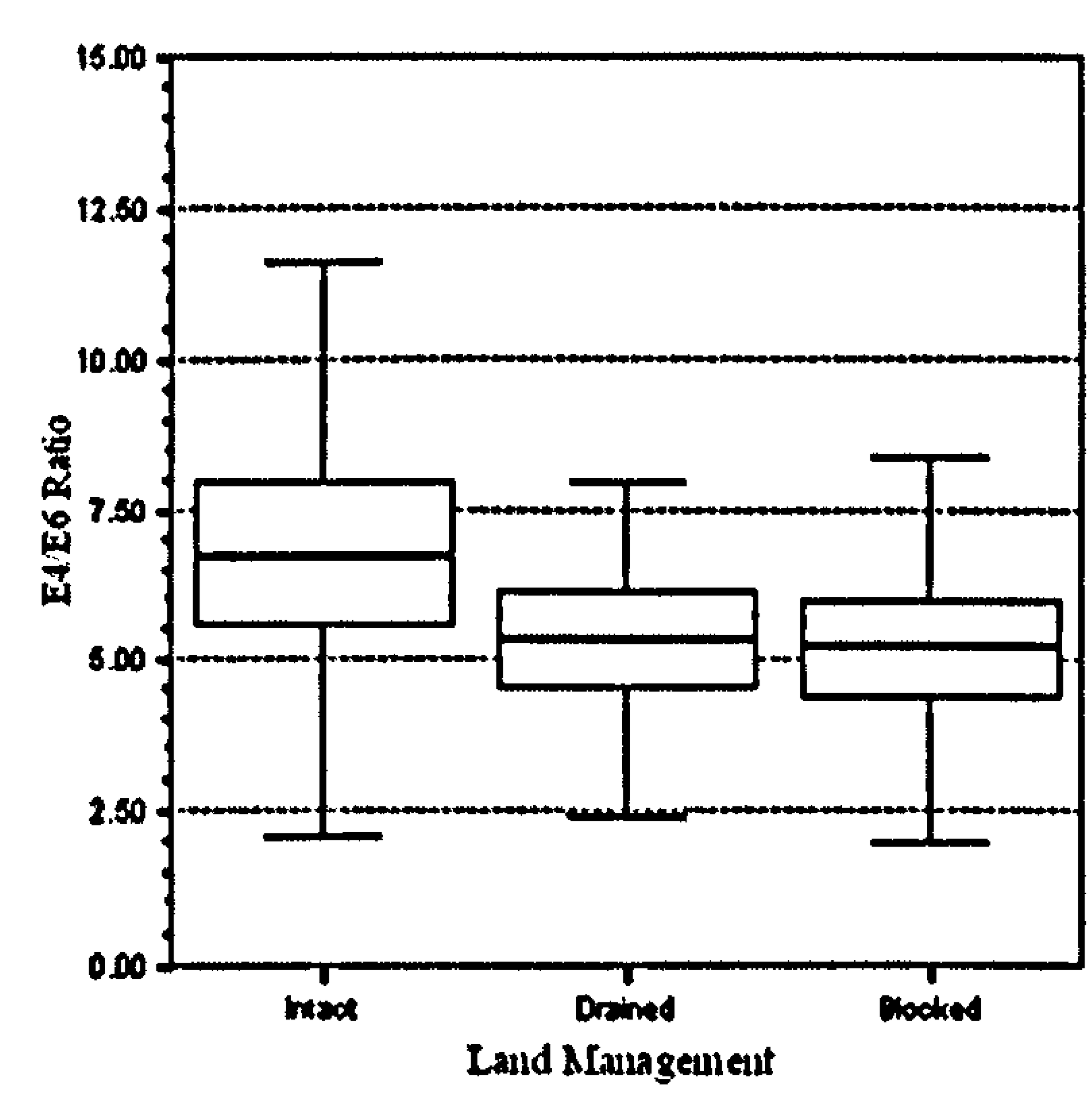


Figure 4.4 A box-plot identifying the spread of the untransformed E4/E6 ratio data for the three treatments.

Note: * = The top of the box represents the third quartile (Q3), which is separated from the bottom of the box (the first quartile (Q1)) by the median. The upper whisker extends to the highest value within the upper limit (upper limit = Q3 + 1.5 *(Q3-Q1), while the lower whisker extends to the lowest value within the lower limit (lower limit = Q1 – 1.5 *(Q3-Q1).

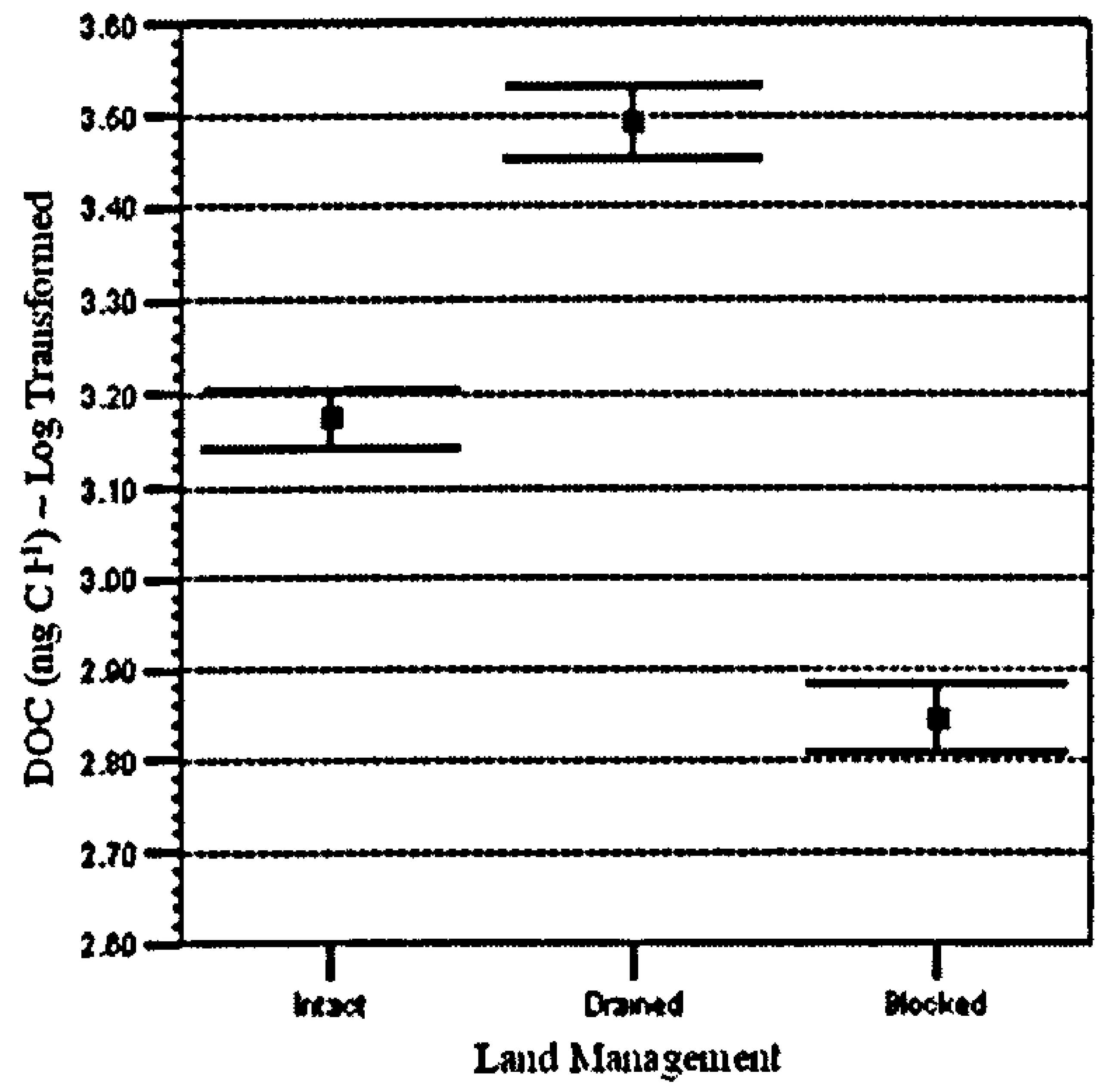


Figure 4.5 Mean DOC for the three treatments, including ± 1 SE of the mean.

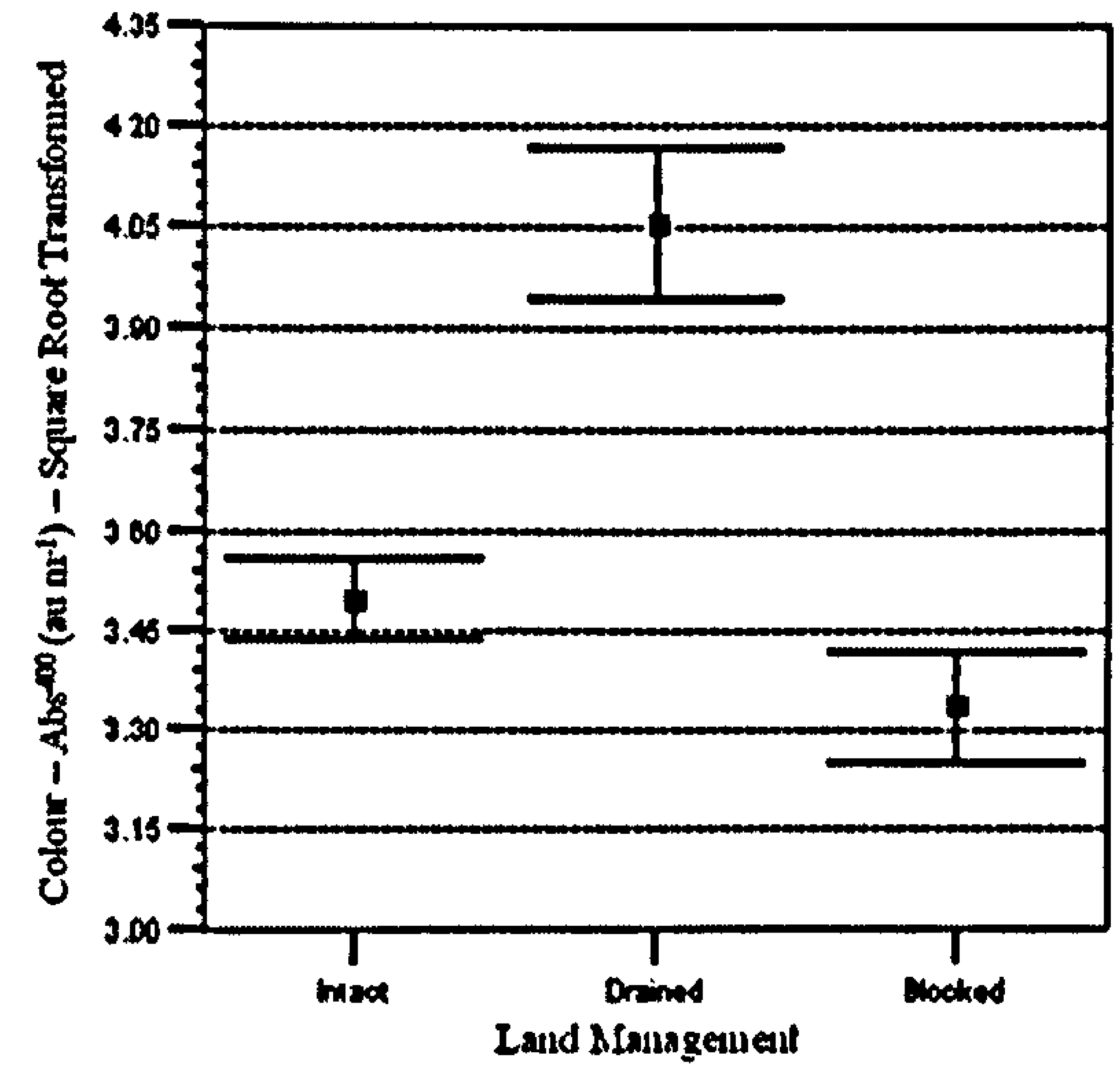


Figure 4.6 Mean colour (Abs^{400}) for the three treatments, including ± 1 SE of the mean.

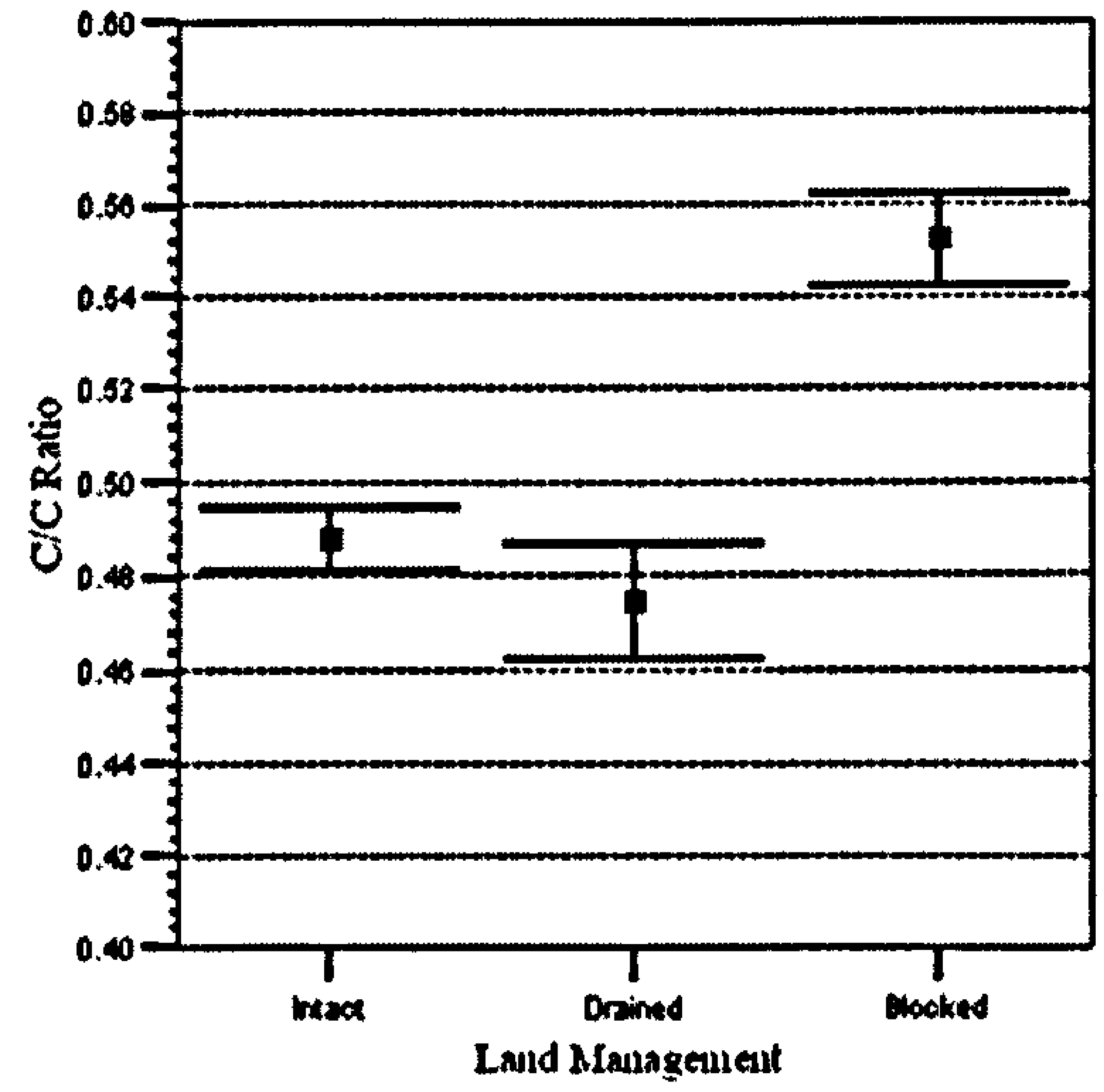


Figure 4.7 Mean C/C ratio for the three treatments, including ± 1 SE of the mean.

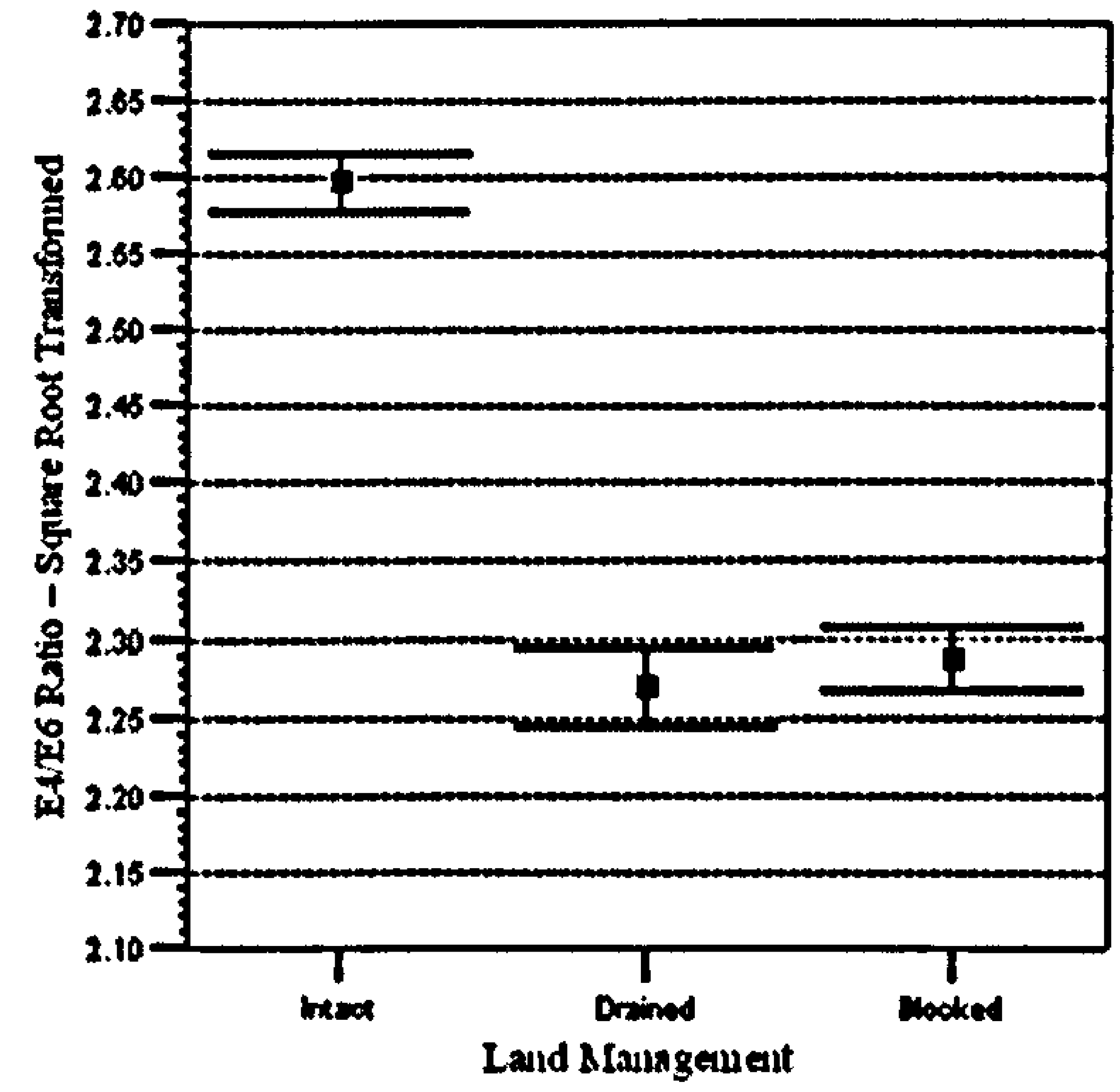


Figure 4.8 Mean E4/E6 ratio for the three treatments, including ± 1 SE of the mean.

	Treatment								
	Intact			Drained			Blocked		
	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
DOC (mg cl^{-1})	23.70	± 1.031	582	31.99	± 1.039	334	16.31	± 1.036	466
Abs^{400} (au m^{-1})	12.22	± 0.004	496	16.43	± 0.013	221	11.11	± 0.007	388
Abs^{436}(au m^{-1})	7.07	±0.002	496	10.27	± 0.008	221	6.98	± 0.004	388
Abs^{465}(au m^{-1})	4.99	± 0.002	496	7.51	± 0.006	221	5.18	± 0.003	388
Abs^{665}(au m^{-1})	0.75	±0.000	496	1.56	± 0.002	221	1.0	±0.001	388
C/C Ratio	0.49	± 0.007	462	0.47	± 0.012	218	0.55	± 0.010	379
E4/E6 Ratio	6.74	± 0.000	495	5.15	± 0.001	220	5.19	± 0.000	381

Table 4.1 Descriptive statistics for the three treatments, including DOC, colour, C/C ratio and E4/E6 ratio, ± 1 SE of the mean and sample size (n).

4.3.2. TEMPORAL VARIABILITY IN DOC AND COLOUR BETWEEN SITES

The DOC and colour variables measured at the three treatments were also analysed on a temporal basis in order to identify any seasonal trends in the relationships observed in Section 4.3.1. ANOVA showed that although there were significant ($p \leq 0.015$) variations in DOC concentration during the sampling period for all three treatments, the differences identified between the sites was sustained, with heightened values observed at the drained site and reduced values at the blocked site relative to the intact site (Table 4.2, Figure 4.9). Assessment of the samples extracted in November however, identified there to be no significant difference (p 0.724) between the intact and drained sites at this point in time. During the sampling period, there were peaks in DOC concentration during February and in August/September, whilst the lowest values observed for all three treatments occurred during October and November.

Analysis of variance of colour for the three sites also showed there to be a significant ($p \leq 0.028$) amount of variation through time at each treatment (Table 4.3, Figure 4.10). Abs^{400} values were very similar at the intact and blocked sites throughout the sampling period, whilst Abs^{400} at the drained treatment remained consistently higher than the other two sites, apart from in November where no significant ($p = 0.175$) difference was found between any of the treatments. Peak Abs^{400} values were evident at the intact and drained treatments in January, which was followed by a second peak at the drained site in August. In contrast however, Abs^{400} values were actually reduced in August at the intact and blocked sites and instead peaked in September, after which time Abs^{400} appeared to reduce.

ANOVA of the C/C ratio for the three treatments identified there to be a significant ($p < 0.001$) amount of variation through time for the intact and blocked sites, whilst at the drained treatment no significant ($p = 0.204$) difference was observed as values remained relatively stable throughout the sampling period (Table 4.4, Figure 4.11). Assessment of how the C/C ratio varied between sites shows that although there is a very close relationship, the values at the blocked site remained consistently higher than both the intact and drained sites, as seen in Section 4.3.1. There appears to be a reduction in the C/C ratio during February and August, which is contrary to the effect seen for DOC and Abs^{400} values at this time. During August, although the C/C ratio was only reduced at the intact and blocked sites, there was no significant (p = 0.395) difference between the three treatments at this time. A large increase in the C/C ratio at the intact and blocked sites occurred during October, which is again in contrast to the pattern observed for DOC and Abs^{400}, and suggests that although lower DOC and Abs^{400} values are observed in the autumn months, the DOC actually contains more colour per carbon unit and thus appears more coloured than DOC released during the summer.

DOC (mg cl^{-1})	Treatment								
	Intact			Drained			Blocked		
Month	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
January	22.50	± 1.099	123	35.99	± 1.105	73	*	*	*
February	24.68	± 1.088	63	40.18	± 1.107	45	13.56	± 1.120	64
March	22.81	± 1.085	63	33.68	± 1.092	50	14.66	± 1.081	61
May	24.15	± 1.071	67	31.71	± 1.069	55	16.57	± 1.098	60
July	27.66	± 1.082	48	34.75	± 1.075	31	17.24	± 1.103	41
August	26.69	± 1.087	46	37.95	± 1.081	26	16.34	± 1.079	49
September	28.30	± 1.083	59	*	*	*	23.62	± 1.100	65
October	20.31	± 1.079	63	*	*	*	15.91	± 1.110	68
November	19.98	± 1.086	50	19.08	± 1.108	54	14.36	± 1.111	58
Mean	**23.70**	**± 1.031**	**582**	**31.99**	**± 1.039**	**334**	**16.31**	**± 1.036**	**466**
ANOVA	$F_{(8, 573)}$ = 1.723, p = 0.015			$F_{(6, 327)}$ = 7.136, p < 0.001			$F_{(7, 458)}$ = 3.258, p = 0.005		

Table 4.2 How DOC varies through time across the three sites, including ± 1 SE of the mean and sample size (n).

Abs^{400}(au m^{-1})	Treatment								
	Intact			Drained			Blocked		
Month	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
January	14.94	± 0.021	128	19.91	± 0.054	59	*	*	*
February	11.08	± 0.040	46	16.75	± 0.101	32	8.84	± 0.063	57
March	11.54	± 0.030	50	17.91	± 0.100	23	9.75	± 0.050	51
May	11.23	± 0.024	54	16.44	± 0.071	37	10.17	± 0.050	53
July	11.24	± 0.043	29	16.76	± 0.125	15	9.17	± 0.048	29
August	9.76	± 0.031	28	20.02	± 0.171	10	8.16	± 0.061	24
September	14.79	± 0.033	57	*	*	*	15.26	± 0.053	59
October	11.34	± 0.023	63	*	*	*	13.09	± 0.038	68
November	8.45	± 0.033	41	10.81	± 0.052	45	12.00	± 0.046	47
Mean	**12.22**	**± 0.004**	**496**	**16.43**	**± 0.013**	**221**	**11.11**	**± 0.007**	**388**
ANOVA	$F_{(8, 487)}$ = 3.291, p = 0.002			$F_{(6, 214)}$ = 2.409, p = 0.028			$F_{(7, 380)}$ = 2.434, p = 0.022		

Table 4.3 How colour (Abs^{400}) varies through time across the three sites, including ± 1 SE of the mean and sample size (n).

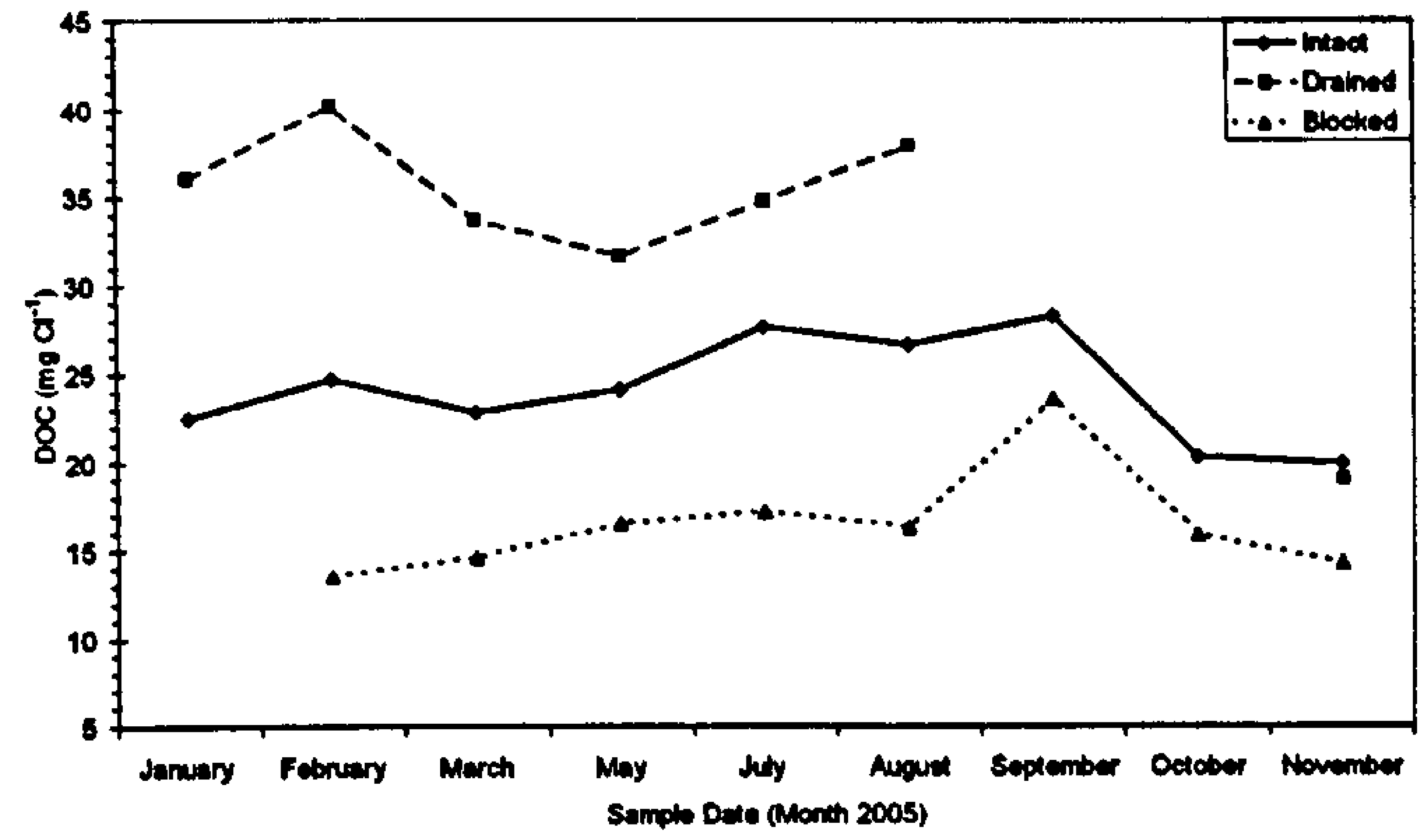


Figure 4.9 How DOC concentration varies between treatments through time.

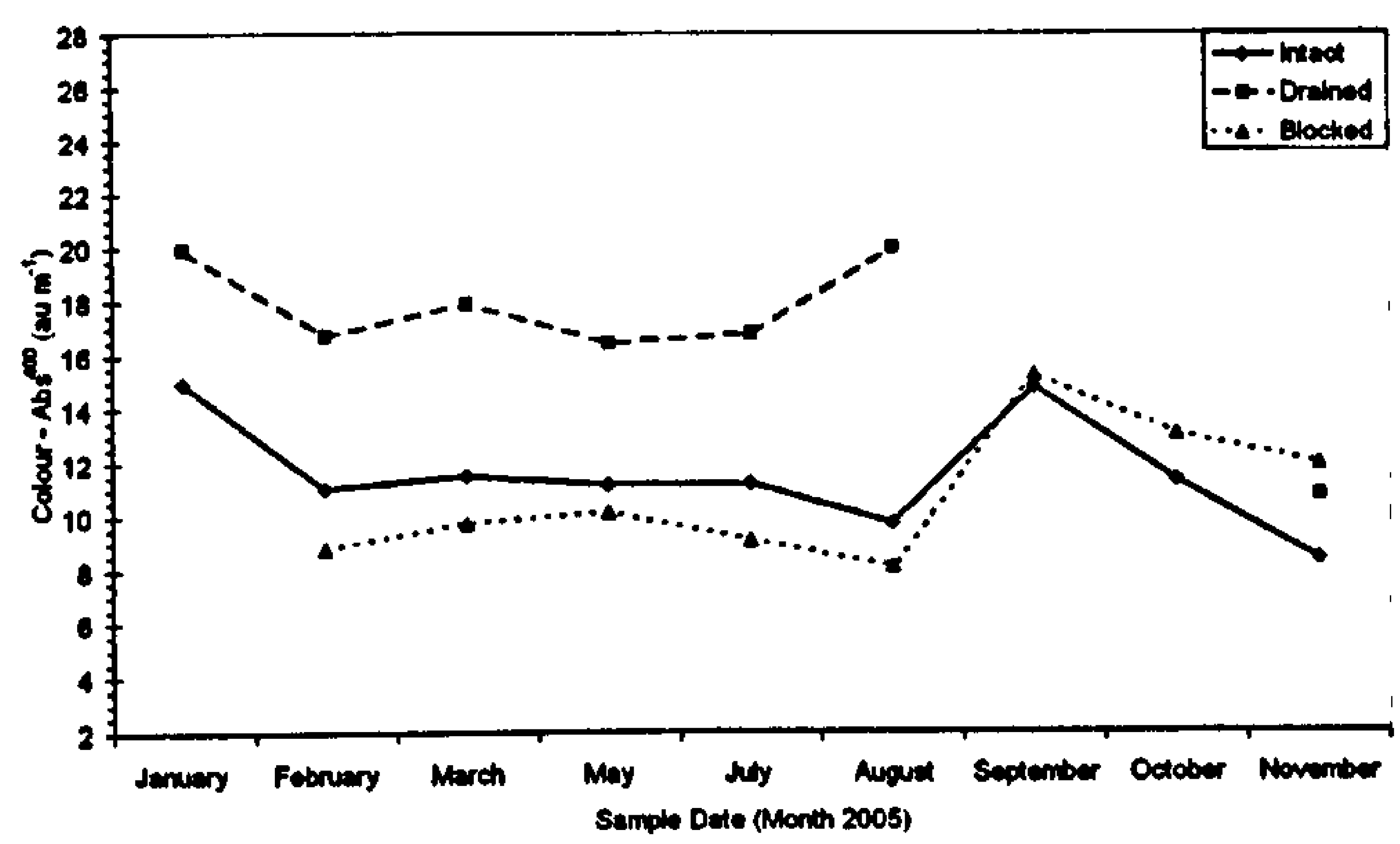


Figure 4.10 How colour (Abs^{400}) levels varies between treatments through time.

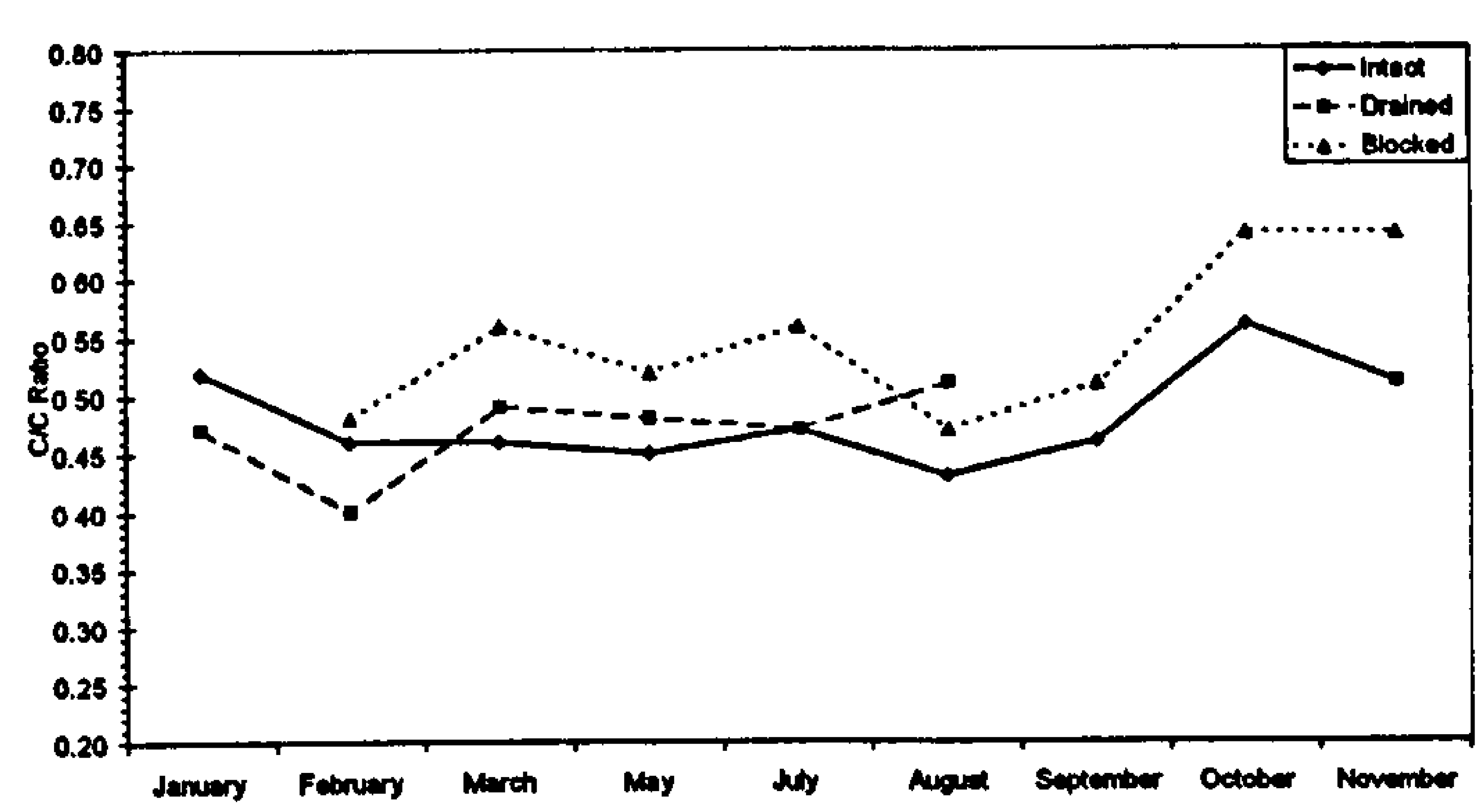


Figure 4.11 How the C/C ratio varies between treatments through time.

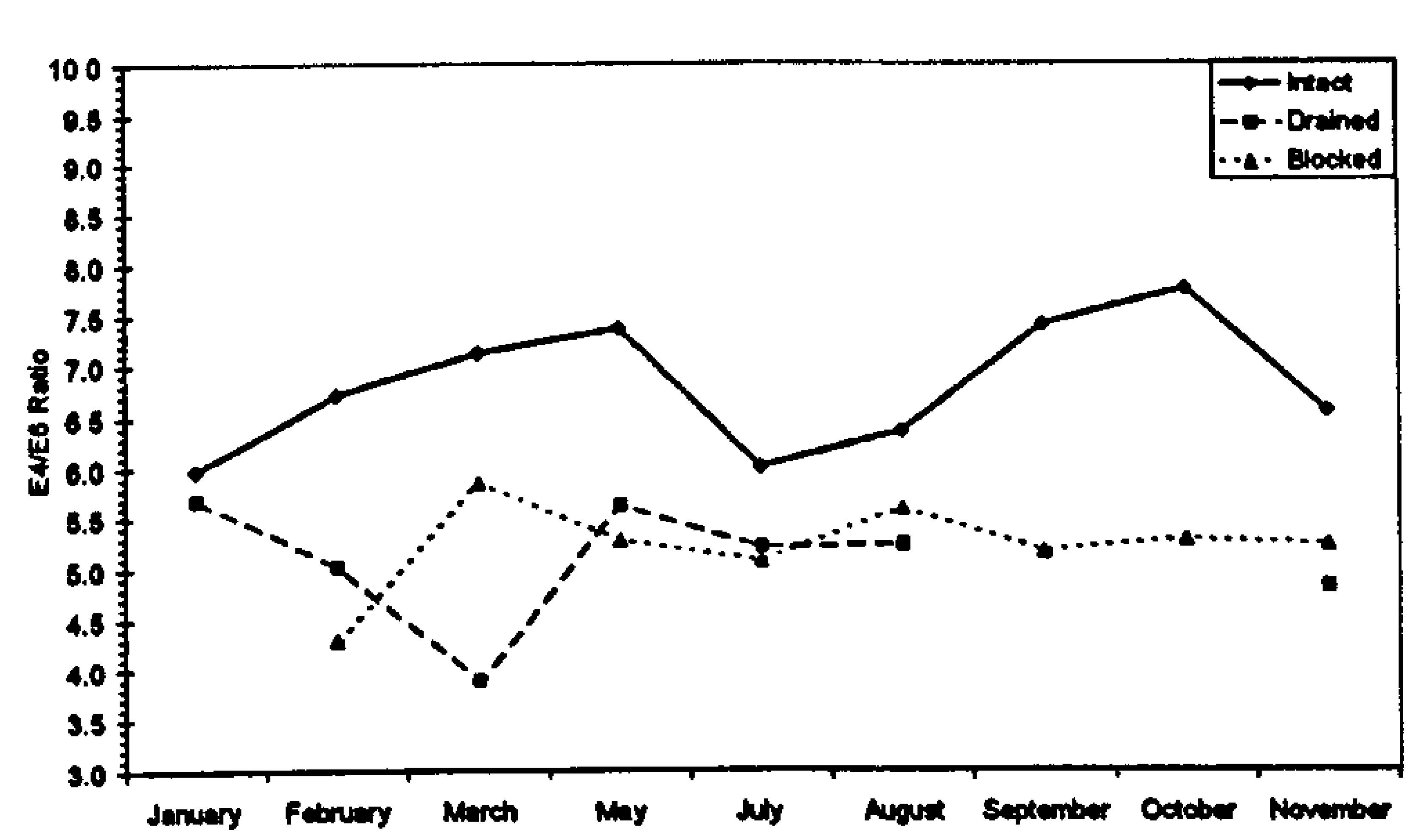


Figure 4.12 How the E4/E6 ratio varies between treatments through time.

C/C Ratio	Treatment								
	Intact			Drained			Blocked		
Month	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
January	0.52	± 0.012	119	0.47	± 0.022	56	*	*	*
February	0.46	± 0.022	46	0.40	± 0.034	32	0.48	± 0.024	56
March	0.46	± 0.019	50	0.49	± 0.032	23	0.56	± 0.024	50
May	0.45	± 0.020	53	0.48	± 0.036	37	0.52	± 0.029	52
July	0.47	± 0.028	27	0.47	± 0.053	15	0.56	± 0.035	28
August	0.43	± 0.030	26	0.51	± 0.037	10	0.47	± 0.037	23
September	0.46	±0.017	51	*	*	*	0.51	± 0.025	58
October	0.56	± 0.016	56	*	*	*	0.64	± 0.024	65
November	0.51	± 0.027	34	0.51	± 0.026	45	0.64	± 0.024	47
Mean	**0.49**	**± 0.007**	**462**	**0.47**	**± 0.012**	**218**	**0.55**	**± 0.010**	**379**
ANOVA	$F(8, 453) = 4.33$ $p < 0.001$			$F(6, 211) = 1.432$ $p = 0.204$			$F(7, 371) = 6.401$ $p < 0.001$		

Table 4.4 How the C/C ratio varies through time across the three sites, including ± 1 SE of the mean and sample size (n).

E4/E6 Ratio	Treatment								
	Intact			Drained			Blocked		
Month	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
January	5.97	± 0.001	128	5.68	± 0.002	59	*	*	*
February	6.72	± 0.002	46	5.03	± 0.004	32	4.30	± 0.003	56
March	7.12	± 0.002	50	3.90	± 0.015	23	5.85	± 0.002	51
May	7.36	± 0.003	54	5.62	± 0.004	37	5.28	± 0.002	49
July	6.00	± 0.003	29	5.22	± 0.004	15	5.08	± 0.002	29
August	6.34	± 0.005	28	5.23	± 0.008	10	5.59	± 0.004	24
September	7.38	± 0.002	57	*	*	*	5.17	± 0.002	59
October	7.74	± 0.003	62	*	*	*	5.28	± 0.001	67
November	6.52	± 0.006	41	4.83	± 0.002	44	5.24	± 0.002	47
Mean	**6.74**	**± 0.000**	**495**	**5.15**	**± 0.001**	**220**	**5.19**	**± 0.000**	**381**
ANOVA	$F(8, 486) = 6.141$ $p < 0.001$			$F(6, 213) = 4.414$ $p = 0.013$			$F(7, 374) = 4.896$ $p < 0.001$		

Table 4.5 How the E4/E6 ratio varies through time across the three sites, including ± 1 SE of the mean and sample size (n).

Figure 4.12 and Table 4.5 indicate that there is a significant ($p \leq 0.01$) amount of variation in the E4/E6 ratio within each site through time, although the heightened ratio observed at the intact site in Section 4.3.1 is maintained throughout the sampling period relative to the lower ratios observed at both the drained and blocked sites. The greatest amount of variation appears at the intact site, where during a general pattern of increasing E4/E6 ratio with time there is a period of decline during July and August, and again in November. The E4/E6 ratio peaks in October at the intact site, which corresponds to the heightened C/C ratio at this time, and indicates that older, more coloured humic material is being sourced. In contrast, at the drained and blocked sites, the E4/E6 ratio generally appears to be more stable, although in March the E4/E6 ratio increases at the blocked site but decreases at the drained site, resulting in a significant (p = 0.002) difference between the two. Changes in the E4/E6 ratio through time at the drained and blocked sites do not appear to correspond as well to variations in the C/C ratio.

4.3.3 DOC AND COLOUR VARIABILITY WITHIN SITES

Comparisons between sites were also made by assessing the variability of DOC and colour with depth along a 40 cm soil profile. ANOVA identified there to be a significant (p <0.001) variation in DOC concentration with soil depth at the intact and drained sites, whilst no significant (p = 0.539) difference was identified between depths at the blocked treatment (Table 4.6). At the intact site there was a general yet significant (p <0.001) increase in DOC concentration with soil depth, with values rising from 11.71 mg C l^{-1} at 0 cm to 36.83 mg C l^{-1} at 40 cm depth (Figure 4.13). A similar trend was observed at the drained site, where DOC increased in concentration from 21.39 mg C l^{-1} at 0 cm to 38.85 mg C l^{-1} at 40 cm. However, the only significant (p <0.001) increase at the drained treatment occurred between 10 and 20 cm depth (Figure 4.14). Figure 4.15 shows that at the blocked site there was very little variability in DOC with soil depth, with values remaining relatively stable at between 15.28 mg C l^{-1} and 18.16 mg C l^{-1} throughout the soil profile.

Analysis of variance of Abs^{400} within the soil profiles of the three sites identified there were significant (p <0.001) differences between depths at both the intact and drained sites (Table 4.7). However, at the blocked site, as with DOC, colour values appeared to be stable with no significant (p = 0.105) differences observed between depths. Figure 4.16 shows that at the intact site, significant (p <0.001) differences were observed between all depths with values increasing with depth from 5.99 au m^{-1} at 0 cm to 15.37 au m^{-1} at 40 cm, although there was a reduction in Abs^{400} from 17.48 au m^{-1} at 10cm to 11.97 au m^{-1} at 20 cm depth. At the drained site there was a similar pattern of increasing Abs^{400} with soil depth, with values rising from 6.54 au m^{-1} to 20.24 au m^{-1}, although there was a significant (p <0.001) reduction between 20 and

40cm (Figure 4.17). Figure 4.18 shows there was little variability in Abs^{400} between depths at the blocked site, with values remaining relatively stable at between 9.11 au m^{-1} to 13.57 au m^{-1}, showing that Abs^{400} was greatly reduced at all depths compared to the intact and drained sites.

In addition to the differences in the C/C ratio between sites identified in Section 4.3.1, there is a high degree of variability within sites. This is manifest in the C/C ratio presented by depth for the intact treatment in Figure 4.19. The amount of colour per carbon unit is clearly not stable between depths. Significant (p <0.02) differences were observed between all depths, with the C/C ratio rising from 0.46 at 0 cm to 0.58 at 10 cm, before falling back to 0.40 at 40 cm. This means that although the pore water at 40 cm depth has the highest DOC concentration, the Abs^{400} at this depth actually remains the same as that of 10 cm. Therefore at 10 cm depth there is nearly 50 % more colour per carbon unit than at 40 cm depth, which means that for a sample with a DOC concentration of 50 mg C l^{-1}, the Abs^{400} at 10 cm would be 29.0 au m^{-1}, whereas at 40 cm it would be 20.0 au m^{-1} (Table 4.8).

Assessment of the C/C ratio for the drained site reveals a very different relationship at depth compared to the intact site (Figure 4.20). The lowest C/C ratio of 0.34 is found at the surface (0 cm) in overland flow, after which the ratio increases significantly (p <0.001) to 0.50 at 5 cm depth, where it remains relatively stable with increasing depth until a significant (p <0.001) reduction from 0.55 to 0.48 between 20 and 40 cm. The differences between the sample subsets demonstrates that, per carbon unit, the DOC in OLF on the drained site contains significantly less colour compared to the rest of the peat depths sampled. The blocked site shows a different pattern to both the intact and drained sites, with Figure 4.21 showing the C/C ratio to be relatively stable at approximately 0.55 at all depths. ANOVA confirmed this, with no significant (p = 0.321) differences found between depths, which means that although there is ultimately less variability between depths compared to the intact and drained sites, the C/C ratio is maintained at a much higher level throughout the soil profile.

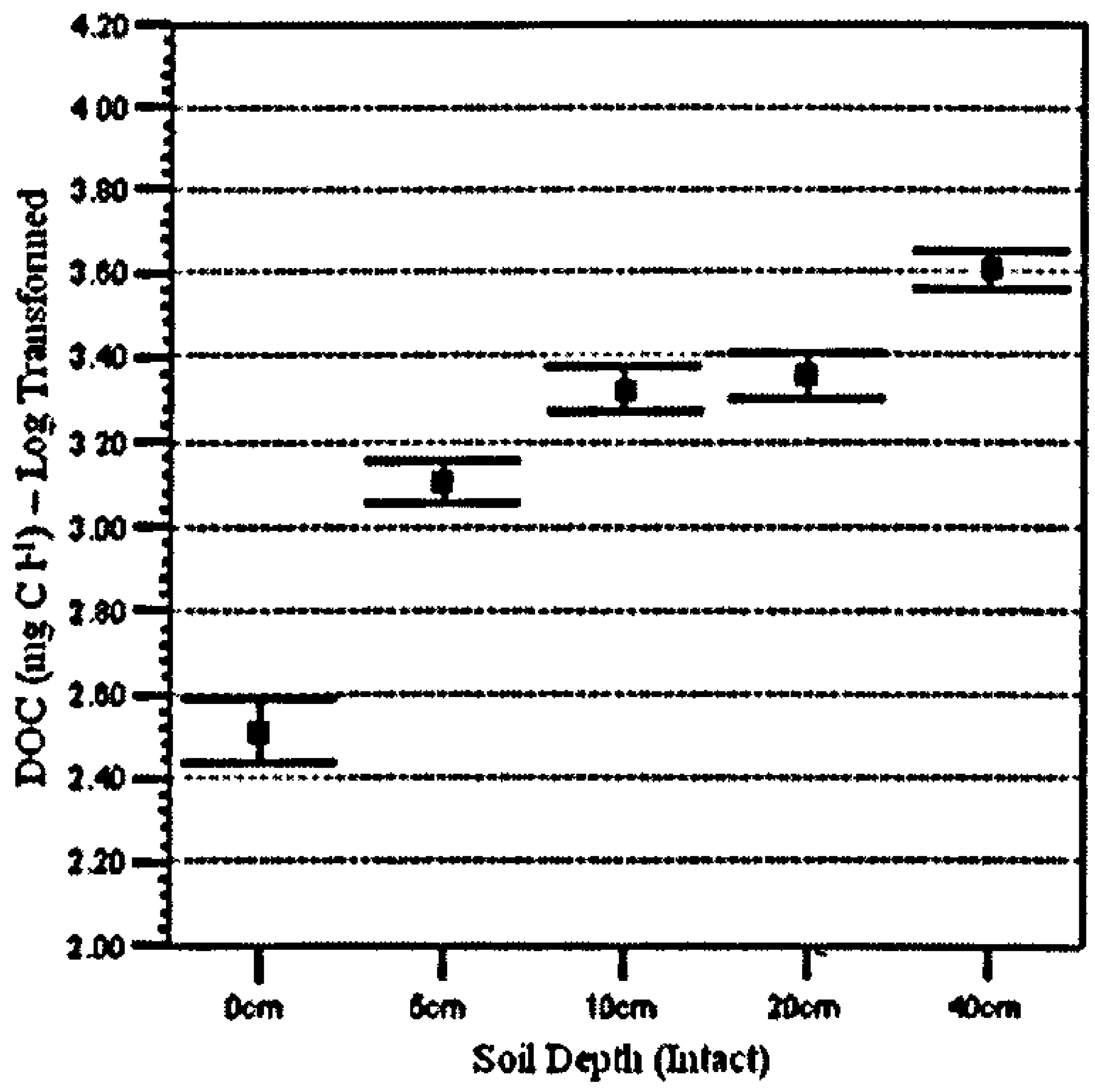


Figure 4.13 Mean DOC values by soil depth for the intact site, including ± 1 SE of the mean.

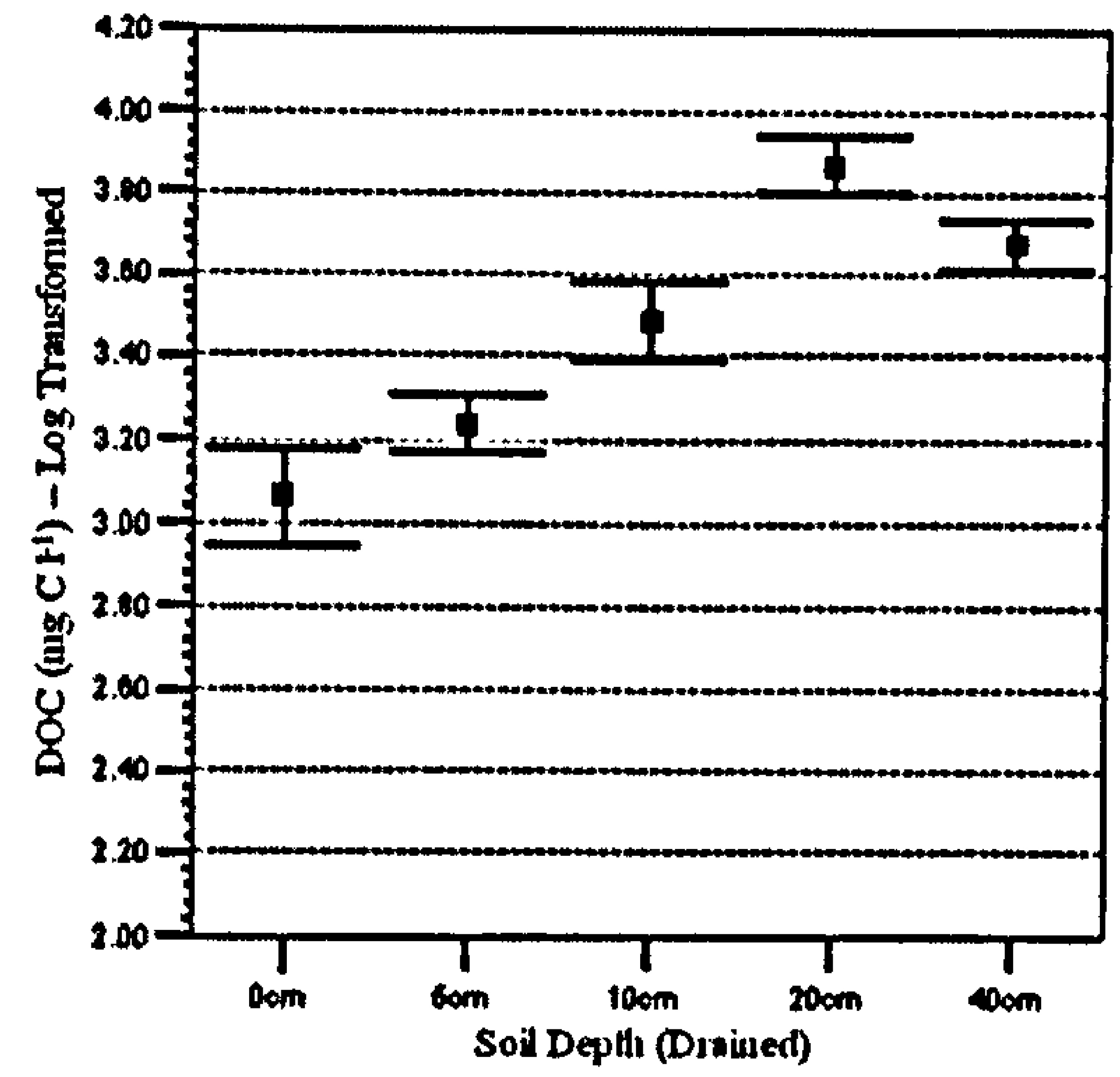


Figure 4.14 Mean DOC values by soil depth for the drained site, including ± 1 SE of the mean.

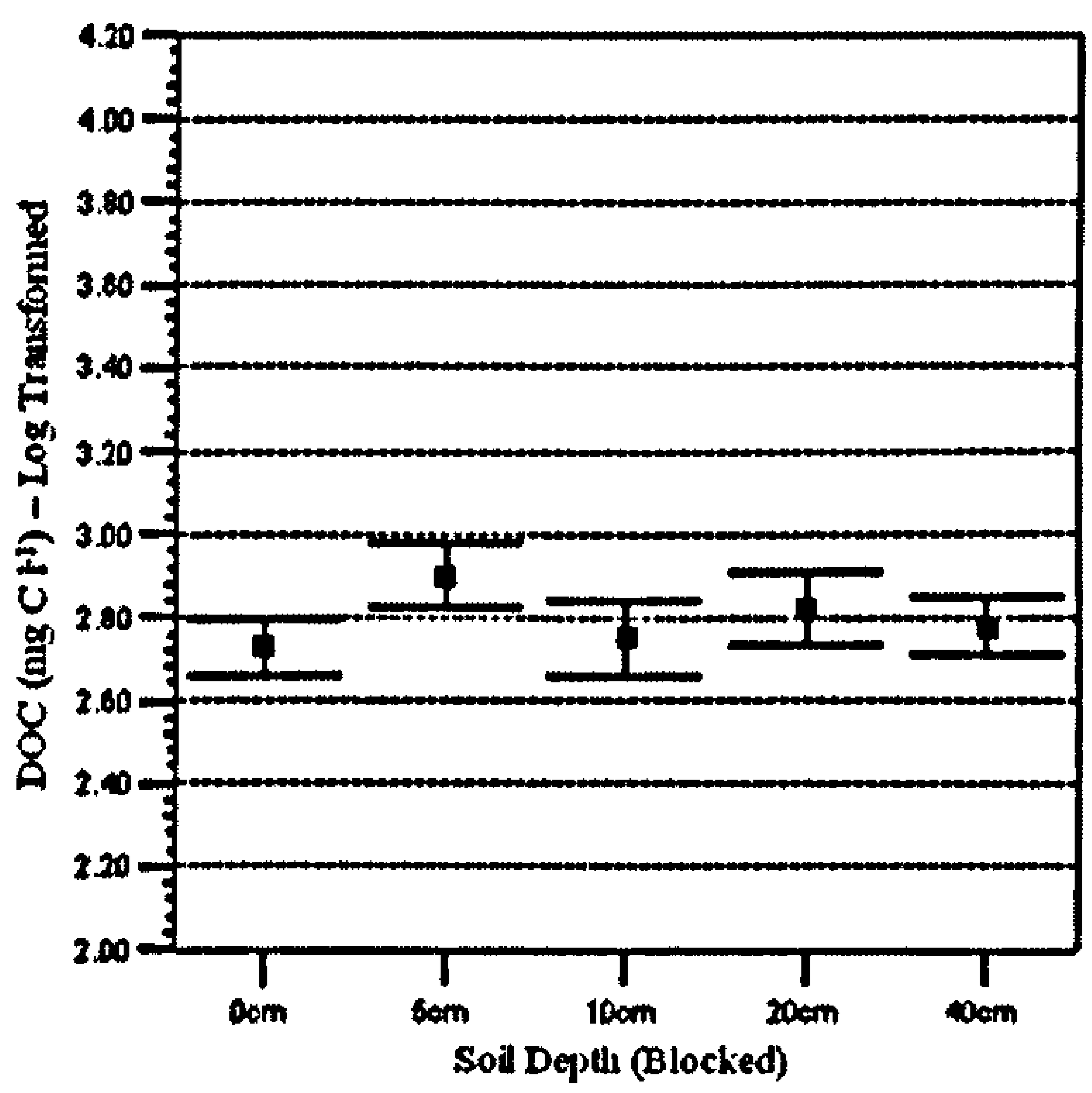


Figure 4.15 Mean DOC values by soil depth for the blocked site, including ± 1 SE of the mean.

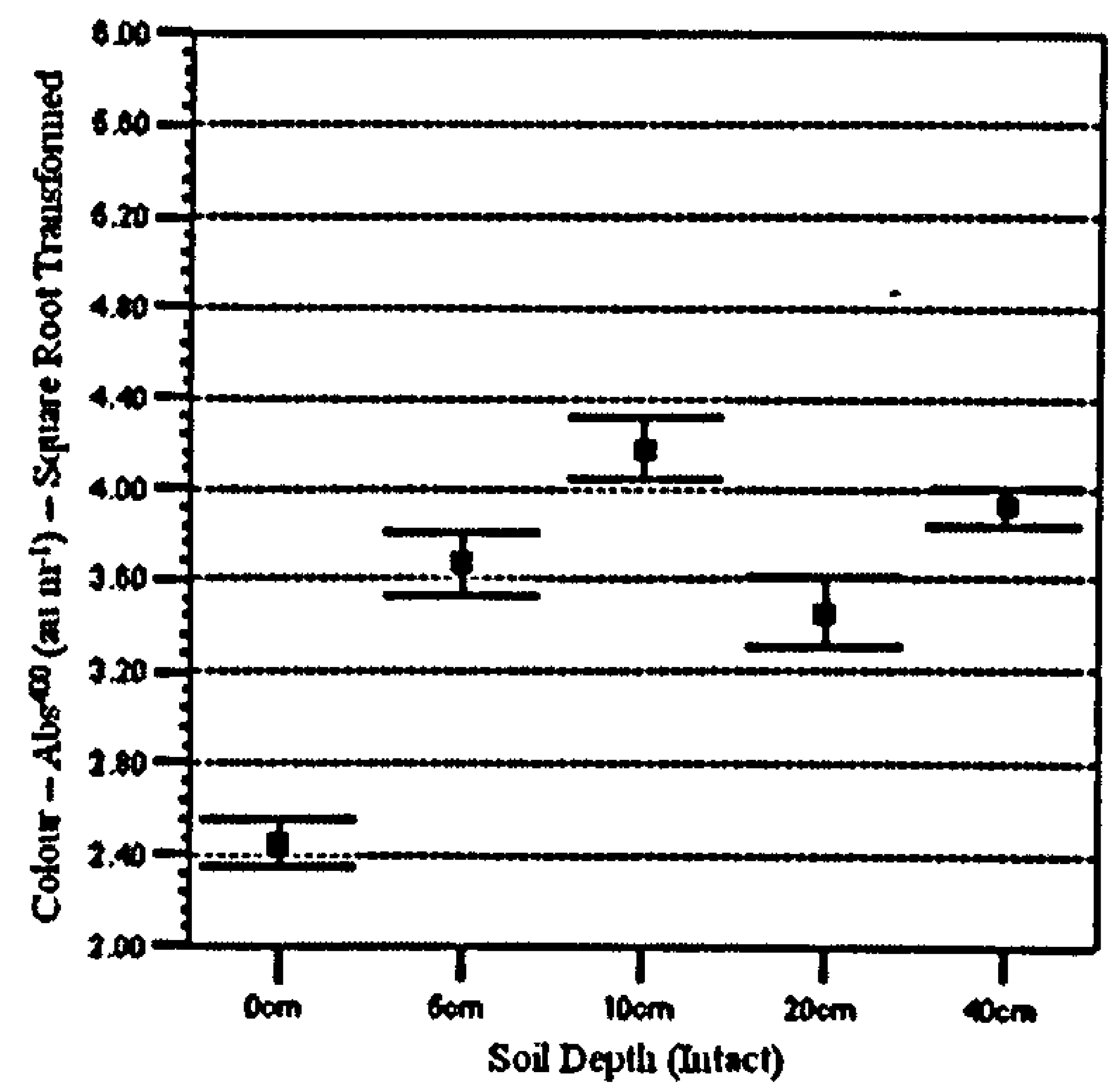


Figure 4.16 Mean colour (Abs^{400}) values by soil depth for the intact site, including ± 1 SE of the mean.

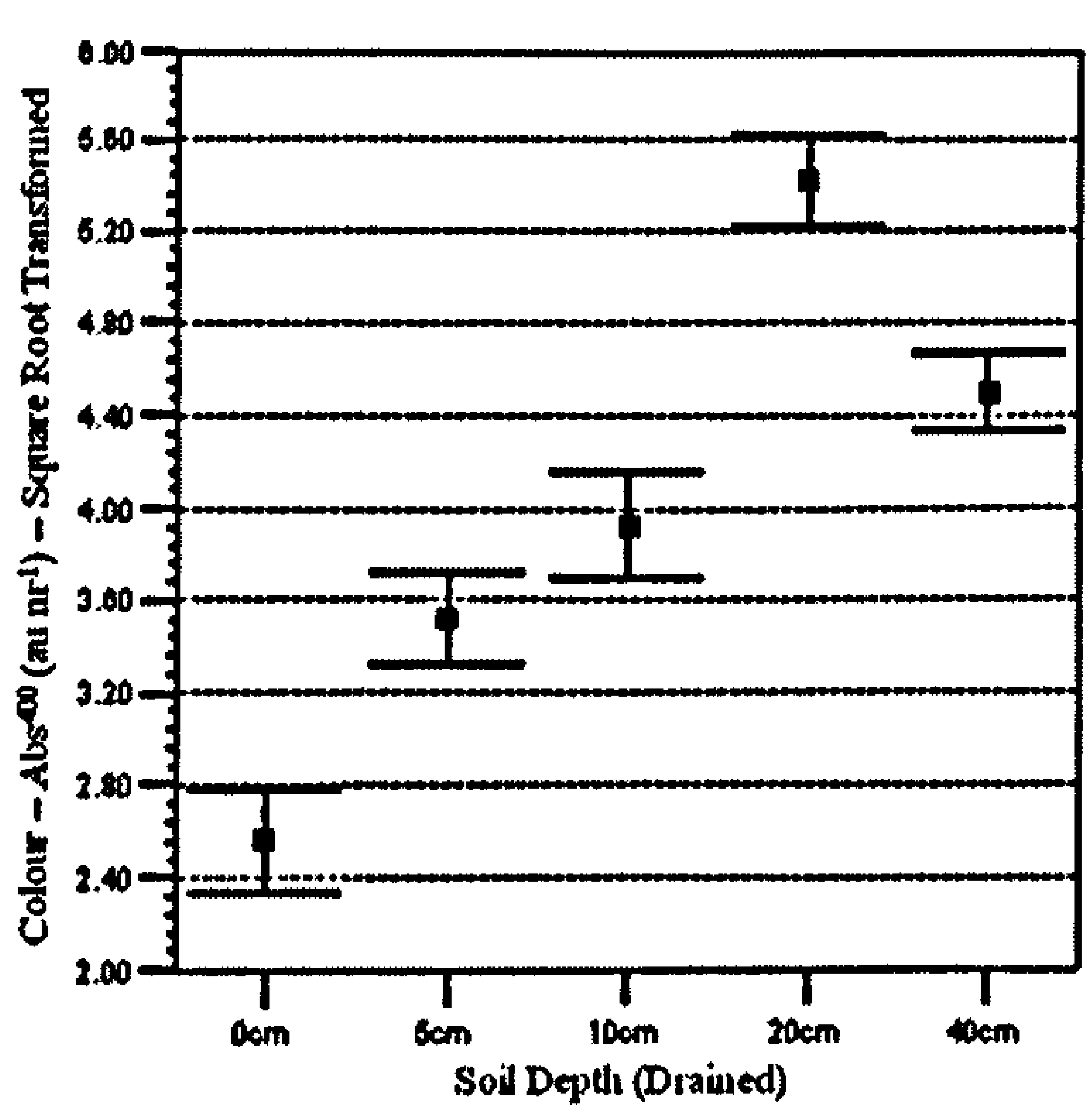


Figure 4.17 Mean colour (Abs^{400}) values by soil depth for the drained site, including ± 1 SE of the mean.

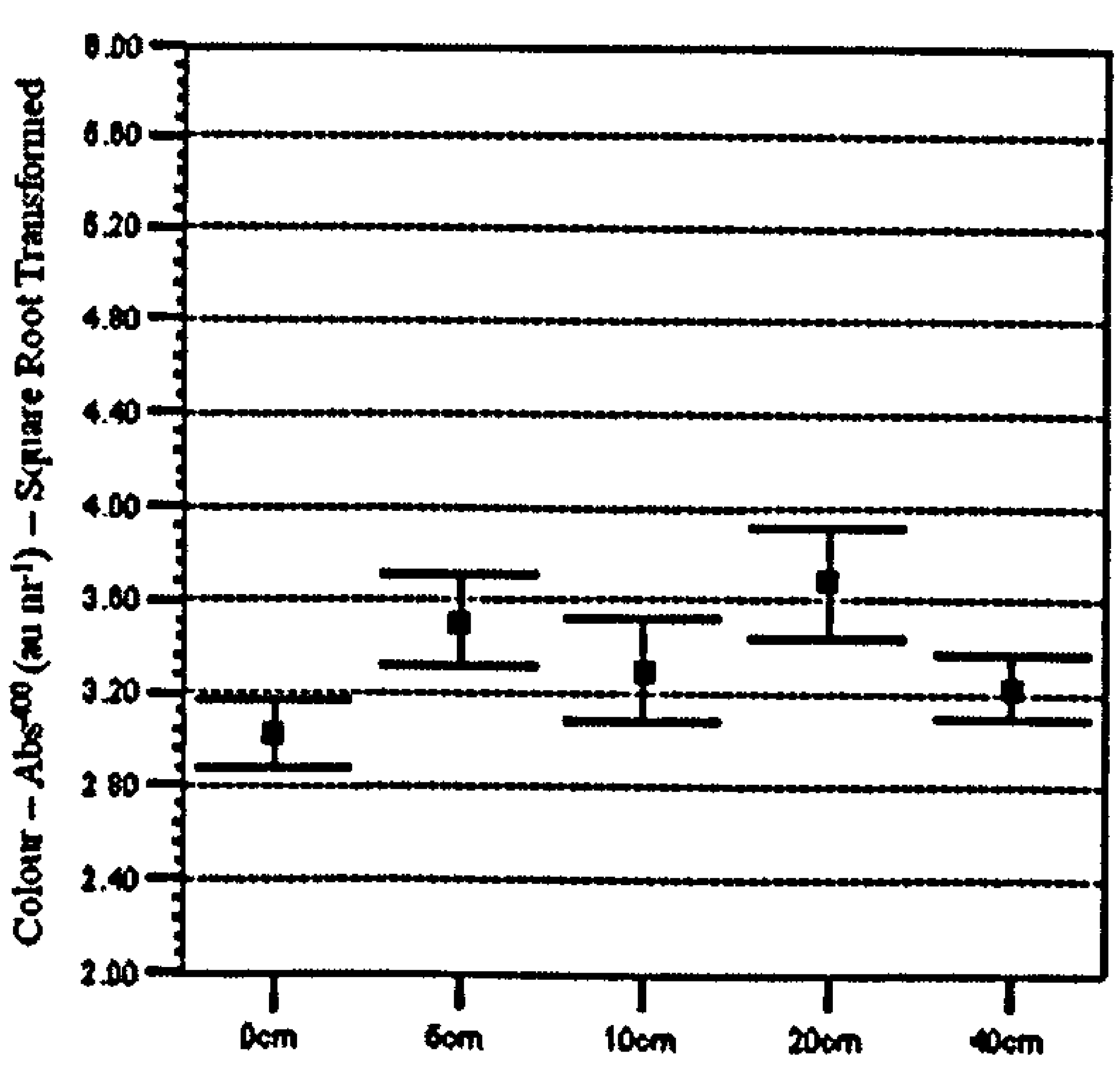


Figure 4.18 Mean colour (Abs^{400}) values by soil depth for the blocked site, including ± 1 SE of the mean.

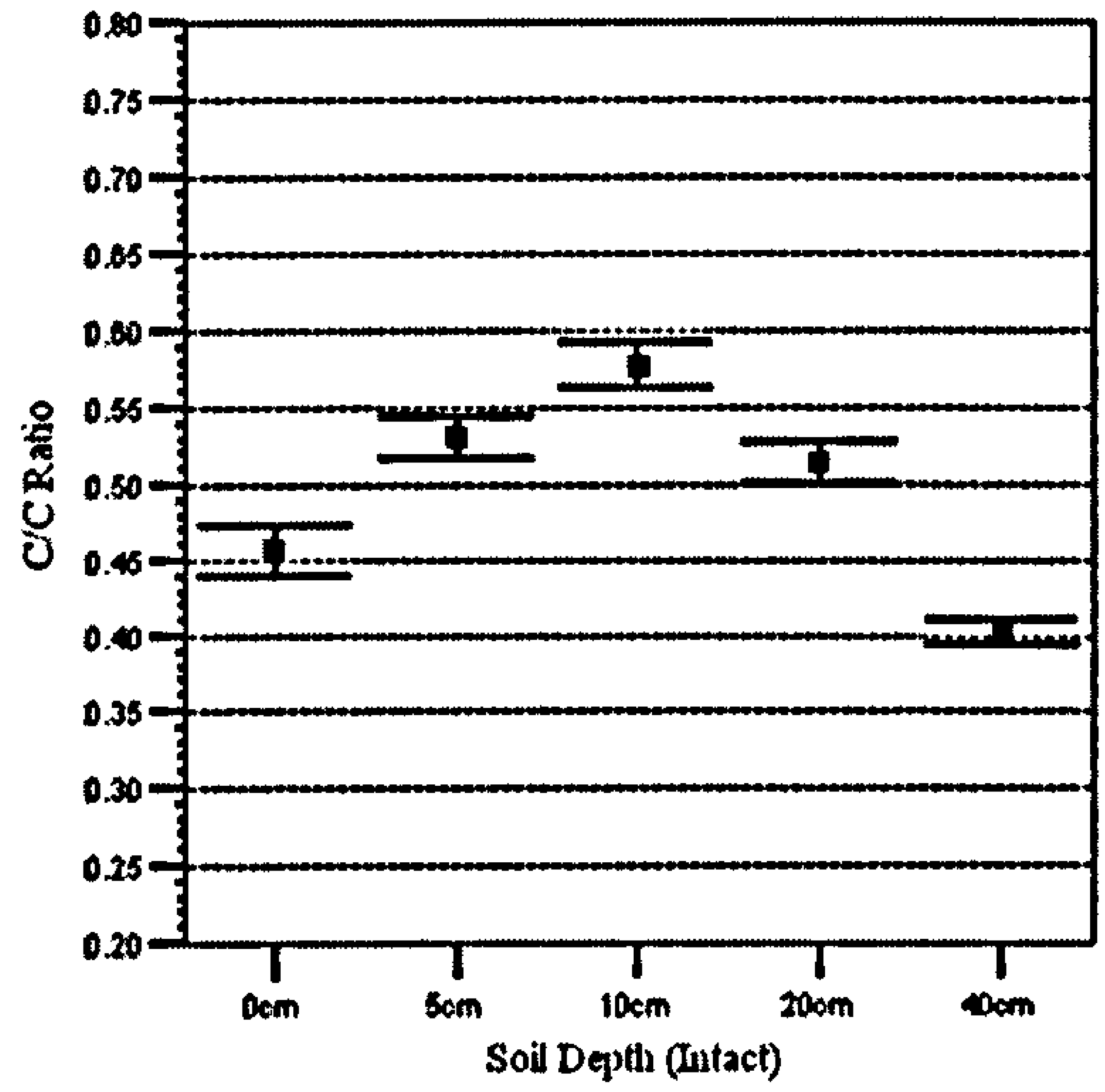


Figure 4.19 Mean C/C ratio by soil depth for the intact site, including ± 1 SE of the mean.

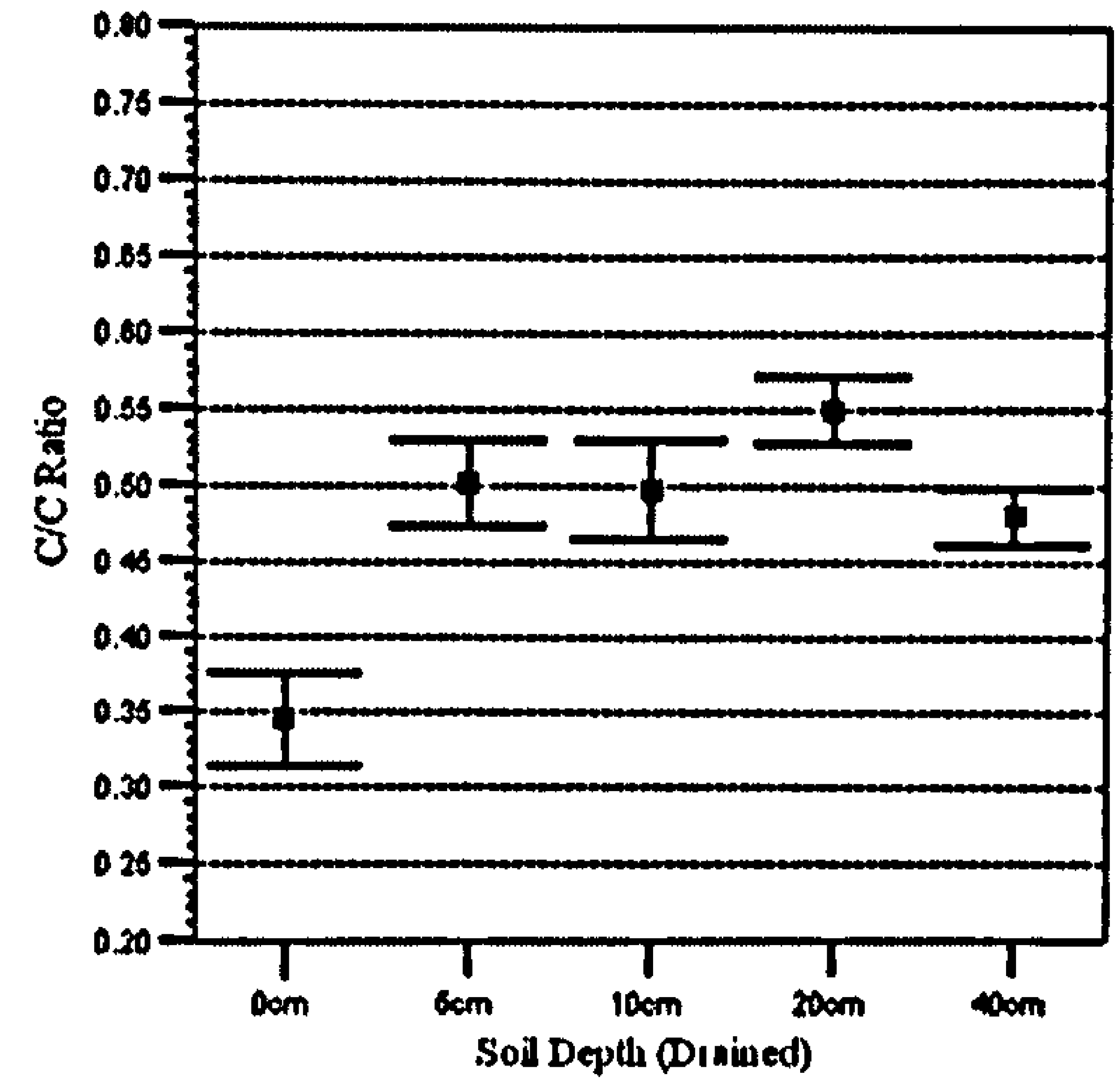


Figure 4.20 Mean C/C ratio by soil depth for the drained site, including ± 1 SE of the mean.

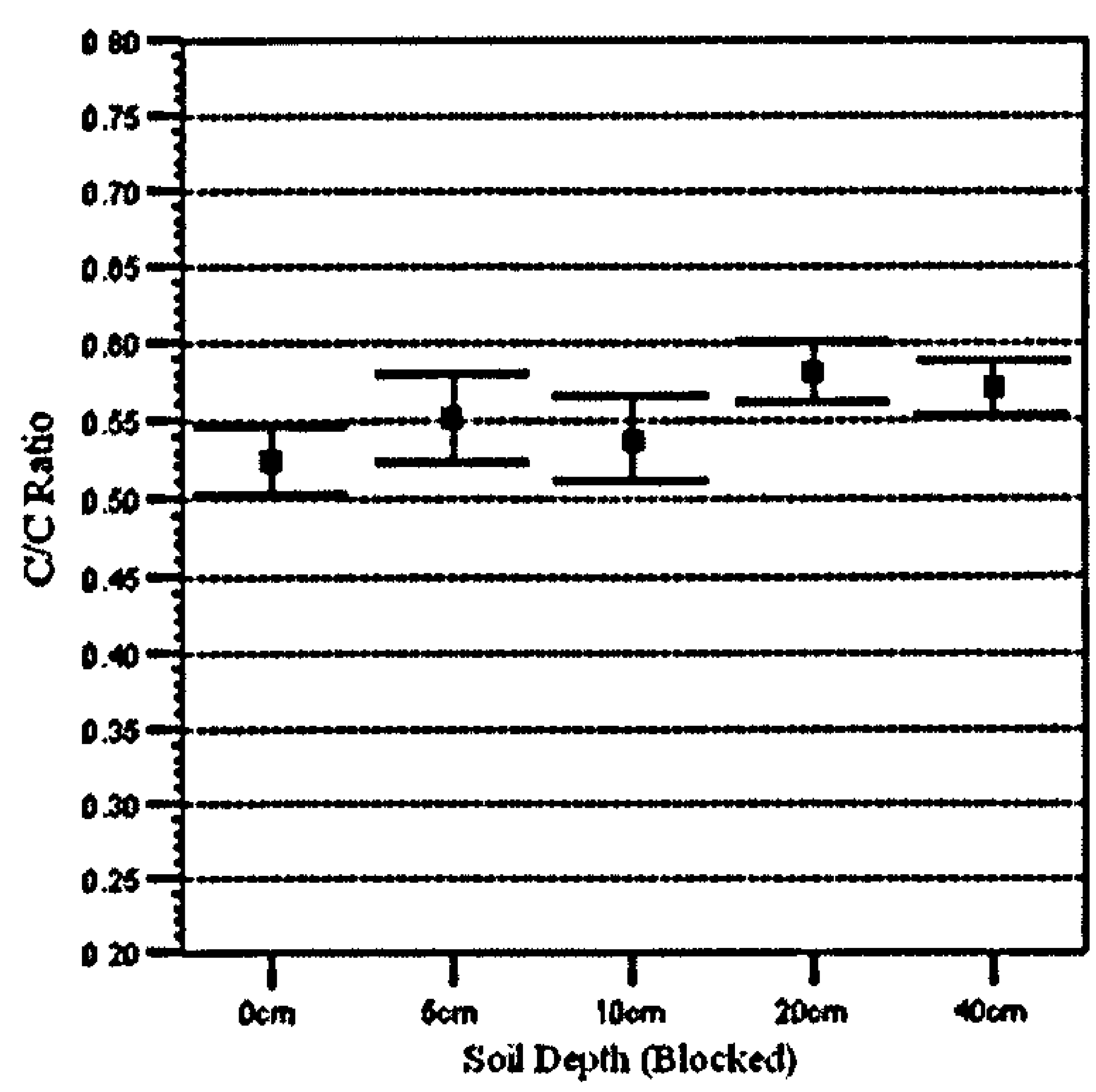


Figure 4.21 Mean C/C ratio by soil depth for the blocked site, including ± 1 SE of the mean.

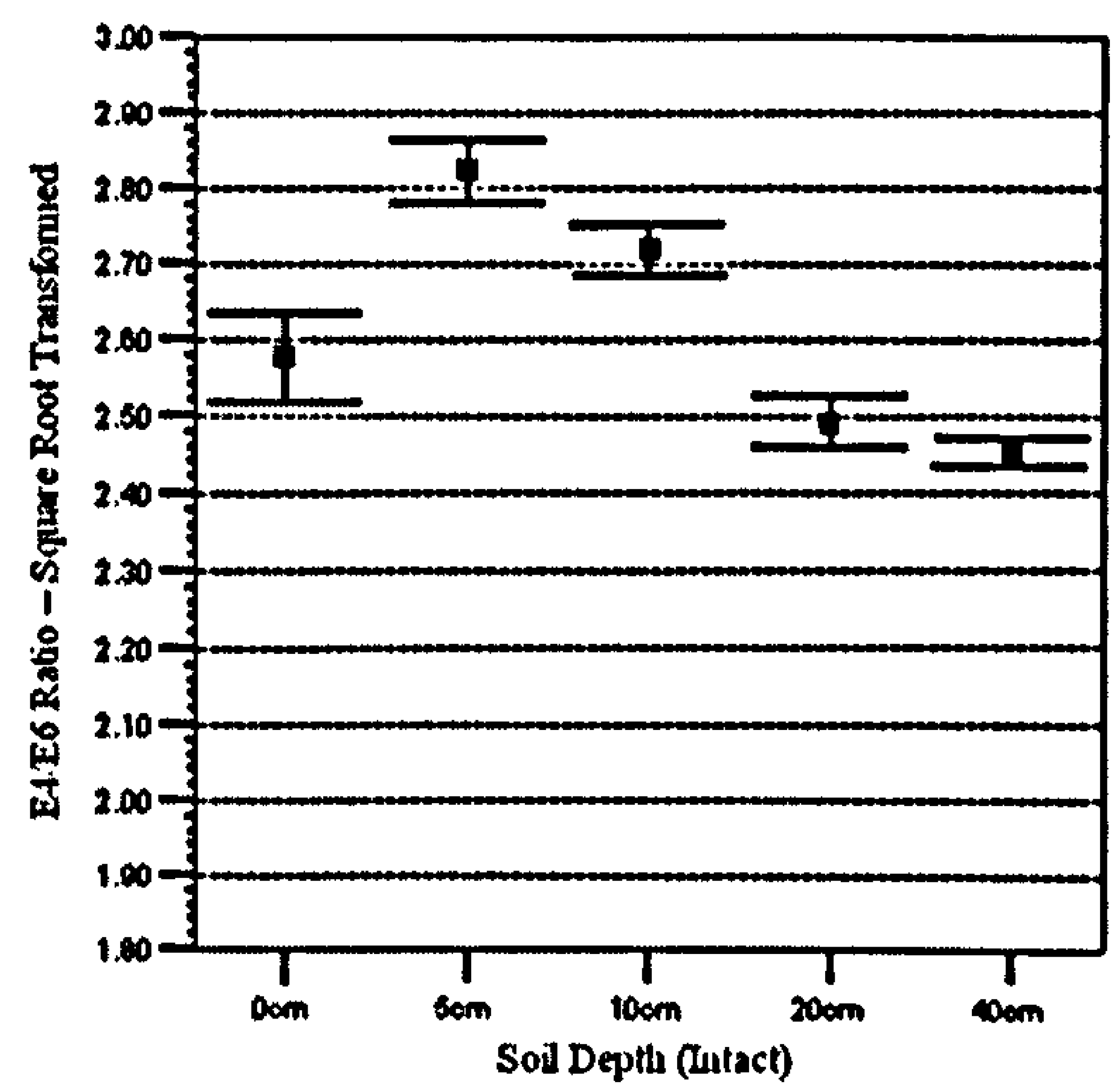


Figure 4.22 Mean E4/E6 ratios by soil depth for the intact site, including ± 1 SE of the mean.

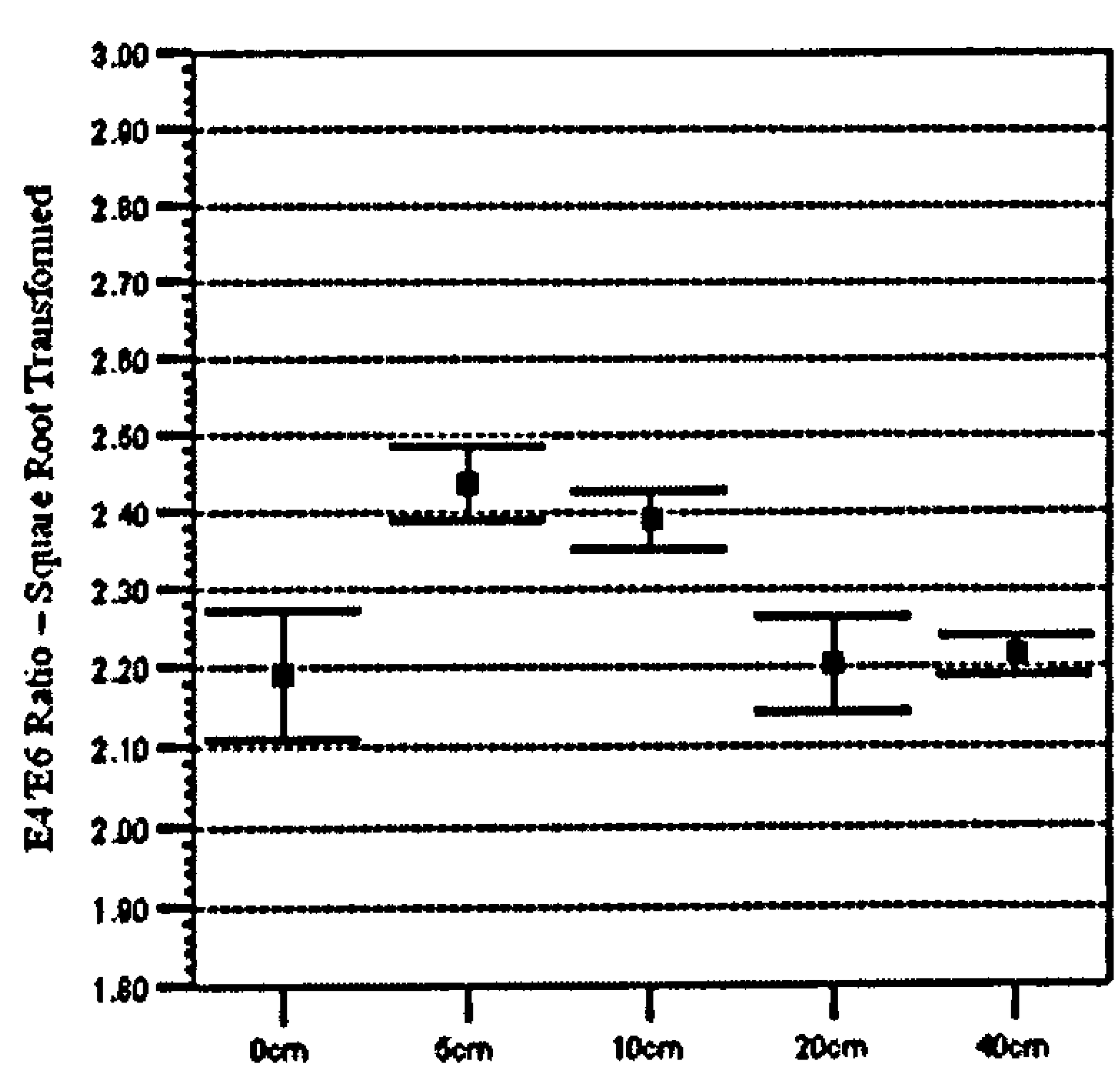


Figure 4.23 Mean E4/E6 ratios by soil depth for the drained site, including ± 1 SE of the mean.

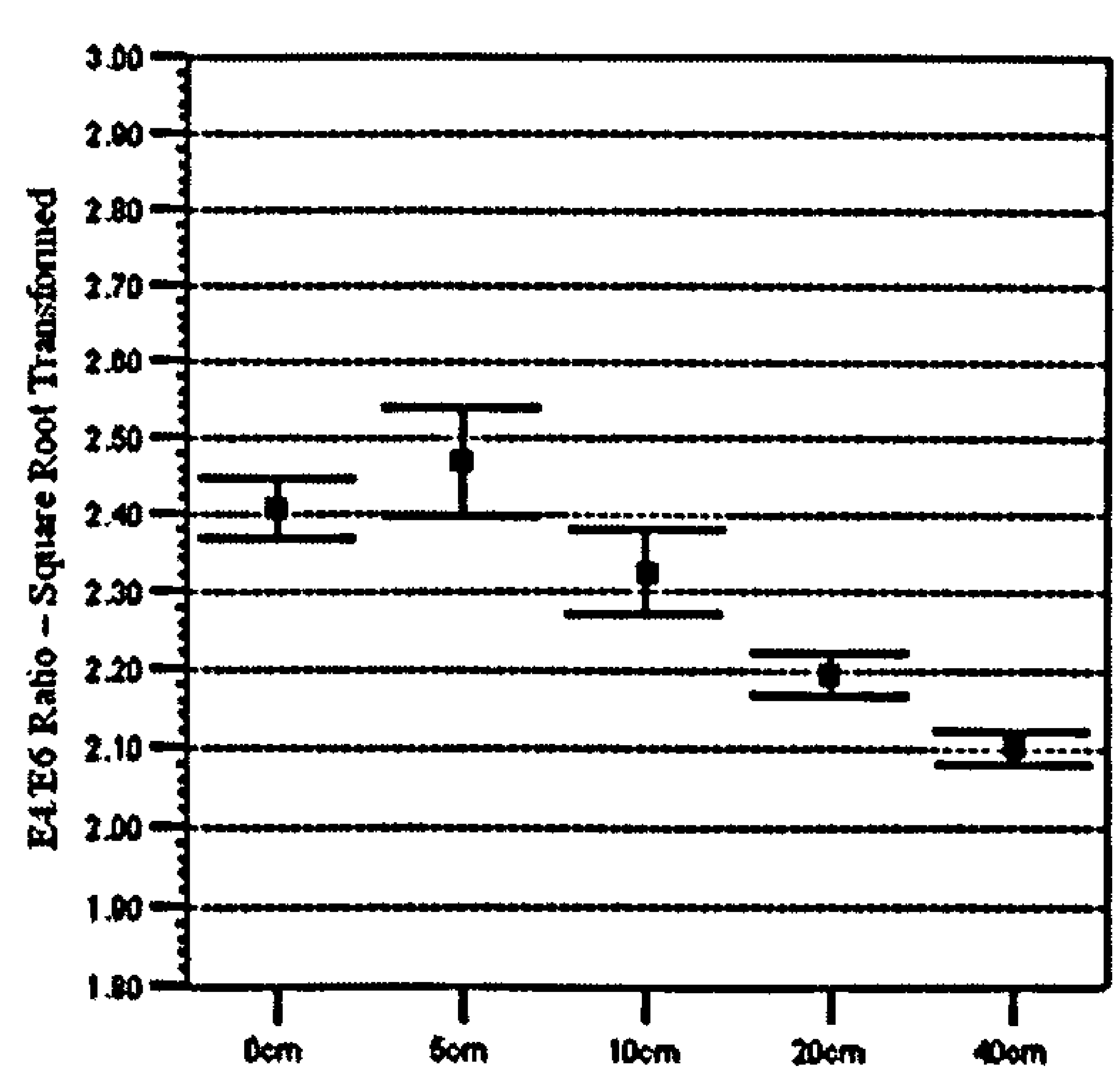


Figure 4.24 Mean E4/E6 ratios by soil depth for the blocked site, including ± 1 SE of the mean.

DOC (mg cl^{-1})	Treatment								
	Intact			Drained			Blocked		
Depth	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**
0 cm	11.71	± 1.073	127	21.39	± 1.124	62	15.28	± 1.075	97
5 cm	22.29	± 1.052	104	25.47	± 1.070	70	18.16	± 1.080	79
10 cm	27.67	± 1.054	109	30.83	± 1.094	45	15.64	± 1.093	89
20 cm	28.59	± 1.054	109	45.76	± 1.066	74	16.82	± 1.093	95
40 cm	36.83	± 1.047	133	38.85	± 1.063	83	16.10	± 1.072	106
Mean	**23.70**	**± 1.031**	**582**	**31.99**	**± 1.039**	**334**	**16.31**	**± 1.036**	**466**
ANOVA	$F(4, 577) = 65.898$ $p < 0.001$			$F(4, 329) = 15.856$ $p < 0.001$			$F(4, 461) = 0.679$ $p = 0.539$		

Table 4.6 Mean DOC values by soil depth for the three sites, including ±1 SE of the mean and sample size (n).

Abs^{400}(au m^{-1})	Treatment								
	Intact			Drained			Blocked		
Depth	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**
0 cm	5.99	± 0.011	115	6.54	± 0.050	46	9.11	± 0.020	92
5 cm	13.47	± 0.018	81	12.42	± 0.041	40	12.32	± 0.037	60
10 cm	17.48	± 0.019	91	15.42	± 0.055	29	10.90	± 0.050	63
20 cm	11.97	± 0.024	97	29.43	± 0.040	50	13.57	± 0.054	83
40 cm	15.38	± 0.006	112	20.24	± 0.028	56	10.48	± 0.019	90
Mean	**12.22**	**± 0.004**	**496**	**16.43**	**± 0.013**	**221**	**11.11**	**± 0.007**	**388**
ANOVA	$F(4,491) = 32.559$ $p < 0.001$			$F(4,216) = 30.065$ $p < 0.001$			$F(4, 383) = 2.080$ $p = 0.105$		

Table 4.7 Mean colour (Abs^{400}) values by soil depth for the three sites, including ±1 SE of the mean and sample size (n).

ANOVA of the E4/E6 ratio by depth for the three land managements shows that there is significant (p <0.001) variation within the soil profile at each site. When overland flow is discounted (as it is likely to be a mixture of water from different depths due to the dominance of saturation-excess overland flow), all three sites show a general decline in E4/E6 ratio with depth (Table 4.9, Figures 4.22 – 4.24). At the intact site, after a significant (p <0.001) increase from 6.63 in OLF to 7.96 at 5 cm, the E4/E6 ratio decreases significantly (p <0.05) with depth until it reaches 20 cm, after which it stabilises. At the drained site there is a significant (p <0.01) increase from 0 cm to 5 cm, after which values tend to decrease with depth, although only a significant (p <0.01) decrease was observed between 10 cm and 20 cm. In contrast, the E4/E6 ratio of OLF for the blocked site was not different to that at 5 or 10 cm depth, but these depths were found to be significantly (p <0.03) higher than that of 20 and 40 cm.

C/C Ratio	Treatment								
	Intact			Drained			Blocked		
Depth	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**
0 cm	0.46	±0.016	110	0.34	±0.031	44	0.52	±0.021	91
5 cm	0.53	±0.014	73	0.50	±0.027	40	0.55	±0.027	57
10 cm	0.58	±0.015	89	0.50	±0.032	29	0.54	±0.027	62
20 cm	0.51	±0.013	78	0.55	±0.022	50	0.58	±0.020	82
40 cm	0.40	±0.008	112	0.48	±0.018	55	0.57	±0.018	87
Mean	**0.49**	**±0.007**	**462**	**0.47**	**±0.012**	**218**	**0.55**	**±0.010**	**379**
ANOVA	$F_{(4, 457)} = 27.208$, $p < 0.001$			$F_{(4, 213)} = 9.467$, $p < 0.001$			$F_{(4, 374)} = 1.176$, $P = 0.321$		

Table 4.8 Mean C/C ratio by soil depth for the three sites, including ±1 SE of the mean and sample size (n).

E4/E6 Ratio	Treatment								
	Intact		n	Drained		n	Blocked		n
Depth	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**	**Mean**	**St Error**	**n**
0 cm	6.63	±0.003	115	4.80	±0.007	45	5.80	±0.002	91
5 cm	7.96	±0.002	80	5.94	±0.002	40	5.81	±0.002	57
10 cm	7.39	±0.001	91	5.70	±0.001	29	5.40	±0.003	62
20 cm	6.21	±0.001	97	4.85	±0.004	50	4.82	±0.001	82
40 cm	6.01	±0.000	112	4.90	±0.001	56	4.41	±0.000	89
Mean	6.74	±0.000	495	5.15	±0.001	220	5.19	±0.000	381
ANOVA	$F_{(4, 490)} = 14.191$, $p < 0.001$			$F_{(4, 215)} = 4.172$, $p < 0.001$			$F_{(4, 377)} = 13.590$, $p < 0.001$		

Table 4.9 Mean E4/E6 ratio by soil depth for the three sites, including ±1 SE of the mean and sample size (n).

4.3.4. DOC AND COLOUR VARIABILITY ACROSS SITE TRANSECTS

In order to further comprehend the influence of drainage and drain blocking on DOC and colour dynamics within the soil profile, it was necessary to assess how the variables were affected across the length of the transect located on each hillslope. At the intact site, DOC and colour values in OLF were relatively low and appeared to be fairly stable across the length of the transect (Figures 4.25 & 4.28). In contrast, Figure 4.26 shows that the DOC in OLF at the drained site was generally elevated across the entire transect, which corresponds well with the 83 % increase observed at this depth relative to the intact site (Tables 4.6 & 4.10). In addition, there appears to be a greater degree of variability in DOC values across the drained transect compared to the intact site, specifically at the two sample points either side of the ditch and at one point located 20 m down-slope of the ditch. In contrast, colour levels in OLF for the drained treatment exhibit a similar trend to those observed at the intact site, and show limited variability near the ditch area (Figure 4.29). However, as observed for the DOC data, there is a peak in colour at approximately 20 m down-slope of the ditch, which helps explain the slightly higher average relative to the intact site (Tables 4.7 & 4.10). The DOC concentration in OLF at the blocked treatment was found to be significantly ($p = 0.01$) higher than that of the intact site, and Figure 4.27 shows that the trend in DOC across the transect appears to mirror that seen at the drained site, albeit to a lesser extent. Meanwhile, Tables 4.7 and 4.10 show that the average colour value for OLF at the blocked treatment was significantly higher than that of both the intact and drained sites, and Figure 4.30 shows a very distinct pattern of disturbance in the area immediately surrounding the ditch, whereby values are clearly reduced relative to those observed further up/down-slope.

Assessment of Figures 4.31 and 4.34 for the C/C and E4/E6 ratios in OLF at the intact site indicate that, although there is a fair amount of variability between stations located along the transect, there is no overriding trend in the data. In contrast, greater variability is observed across the drained transect with both the C/C and E4/E6 ratios appearing reduced in the area nearest the ditch, which relates well to the significantly lower average observed for both ratios relative to the intact site (Figures 4.32 & 4.35 and Tables 4.8 – 4.10). Figure 4.33 shows the C/C ratio at the blocked site exhibits a stronger, yet more confined pattern of drawdown in the area immediately surrounding the ditch, with values further up/down-slope appearing elevated. This corresponds well with the significantly higher C/C ratio observed for this treatment relative to the intact and drained sites (Tables 4.8 & 4.10). In Figure 4.36, no obvious difference in the E4/E6 ratio in OLF along the blocked transect was observed when compared to the intact site, with both transects exhibiting similar levels of variability; however, the average E4/E6 ratio at the blocked site was significantly ($p = 0.016$) lower.

At 5 cm, Figures 4.37 and 4.38 show a fairly similar trend in DOC is observed across the intact and drained transects, with only a small degree of variability evident between stations and no significant difference observed between the sites at this depth (Tables 4.6 & 4.10). In contrast, Figure 4.39 shows that DOC appears to be reduced at the stations immediately down-slope of the ditch at the blocked site, which corresponds well with the significantly ($p = 0.028$) lower average compared to the intact and drained sites. Analysis of colour at 5 cm depth shows there is little variability between sample stations across all three transects, and no significant differences were observed between sites (Figures 4.40 – 4.42, and Tables 4.7 & 4.10). However, colour levels appeared slightly reduced in the first few metres down-slope of the ditch at the drained and blocked sites, suggesting they may be elevated elsewhere along the transect. It can be seen in Figures 4.43 – 4.45 that, although no significant difference was observed in the C/C ratio at 5 cm depth between the three sites, there appears to be a distinct area of disturbance immediately down-slope of the ditch at the blocked site, whereas across the drained transect the C/C ratio generally appears more variable. Figures 4.46 – 4.48 show that, apart from a peak in the E4/E6 ratio at about 40 m down-slope of the ditch at the blocked site, the three transects generally exhibit the same amount of variation between stations. Nonetheless, the E4/E6 ratio was found to be significantly lower at the drained and blocked sites relative to the intact treatment (Tables 4.9 & 4.10).

	Treatment Comparisons		
DOC (mg cl^{-1})	**Intact v Drained**	**Intact v Blocked**	**Drained v Blocked**
0 cm	<u>≤0.001</u>	<u>0.01</u>	<u>0.016</u>
5 cm	0.111	<u>0.028</u>	<u>0.01</u>
10 cm	0.280	<u>≤0.001</u>	<u>≤0.001</u>
20 cm	<u>≤0.001</u>	<u>≤0.001</u>	<u>≤0.001</u>
40 cm	0.482	<u>≤0.001</u>	<u>≤0.001</u>
Abs^{400}(au m^{-1})			
0 cm	0.653	<u>0.001</u>	0.075
5 cm	0.541	0.484	0.961
10 cm	0.363	<u>0.001</u>	0.057
20 cm	<u>≤0.001</u>	0.426	<u>≤0.001</u>
40 cm	<u>0.002</u>	<u>≤0.001</u>	<u>≤0.001</u>
C/C Ratio			
0 cm	<u>0.002</u>	<u>0.019</u>	<u>≤0.001</u>
5 cm	0.328	0.514	0.212
10 cm	<u>0.013</u>	0.201	0.389
20 cm	0.167	<u>0.007</u>	0.322
40 cm	<u>≤0.001</u>	<u>≤0.001</u>	<u>0.001</u>
E4/E6 Ratio			
0 cm	<u>≤0.001</u>	<u>0.016</u>	<u>0.019</u>
5 cm	<u>≤0.001</u>	<u>≤0.001</u>	0.687
10 cm	<u>≤0.001</u>	<u>≤0.001</u>	0.448
20 cm	<u>≤0.001</u>	<u>≤0.001</u>	0.916
40 cm	<u>≤0.001</u>	<u>≤0.001</u>	<u>0.001</u>

Table 4.10 Significance values for DOC, colour (Abs^{400}), C/C and E4/E6 ratios by depth when individual sites are compared.

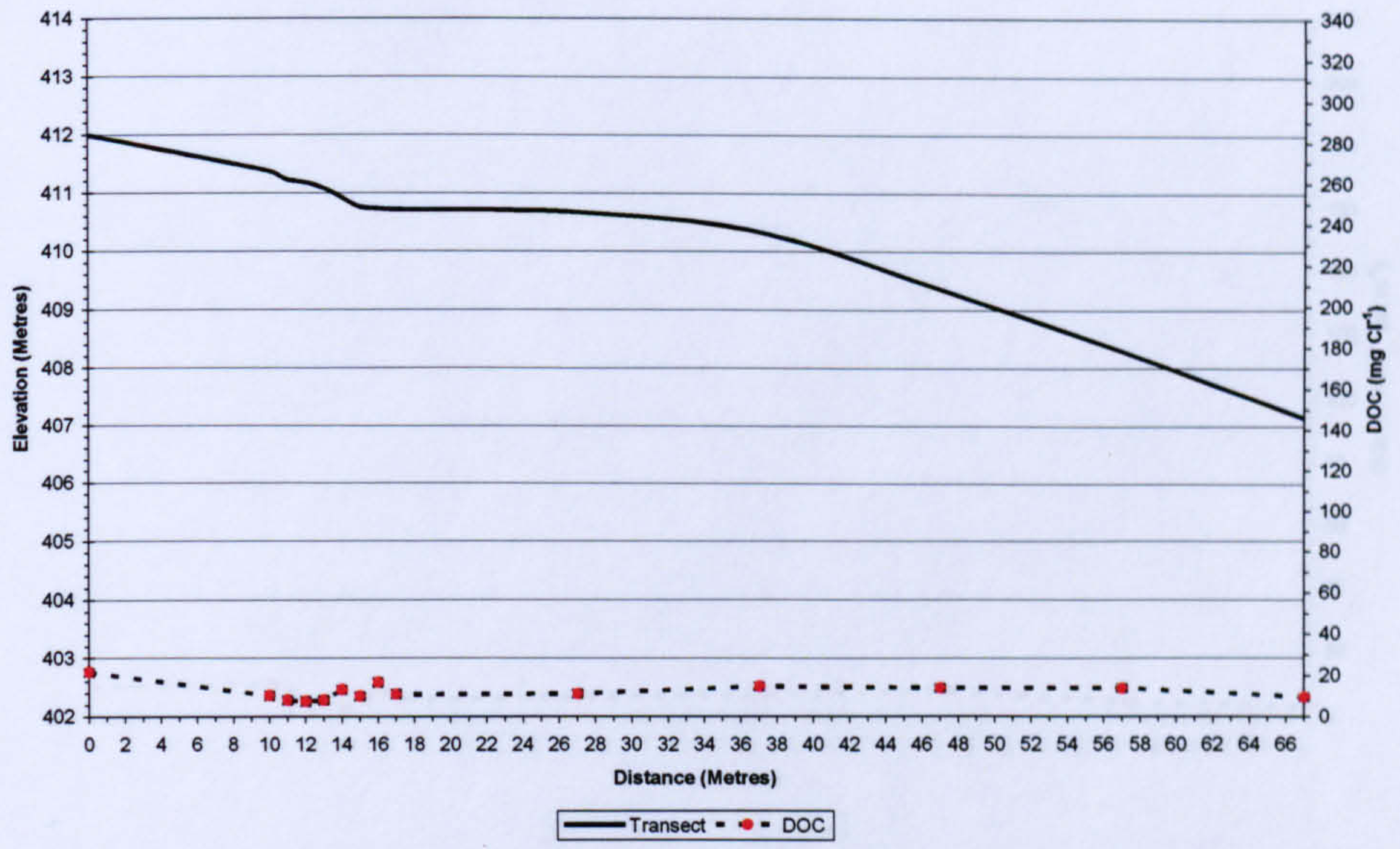


Figure 4.25 How DOC in OLF varies across the intact transect. Vertical bars represent the SE mean.

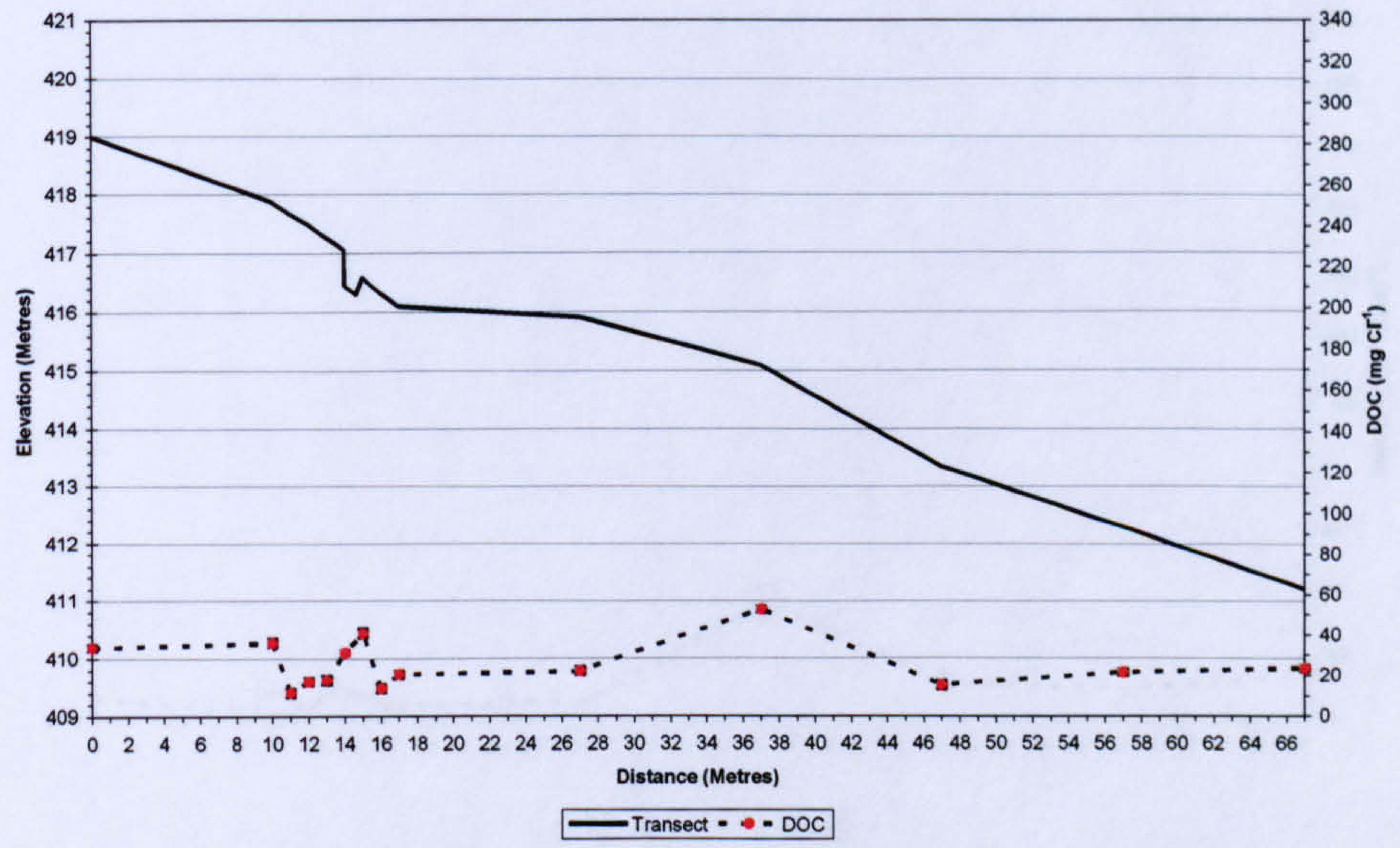


Figure 4.26 How DOC in OLF varies across the drained transect. Vertical bars represent the SE mean.

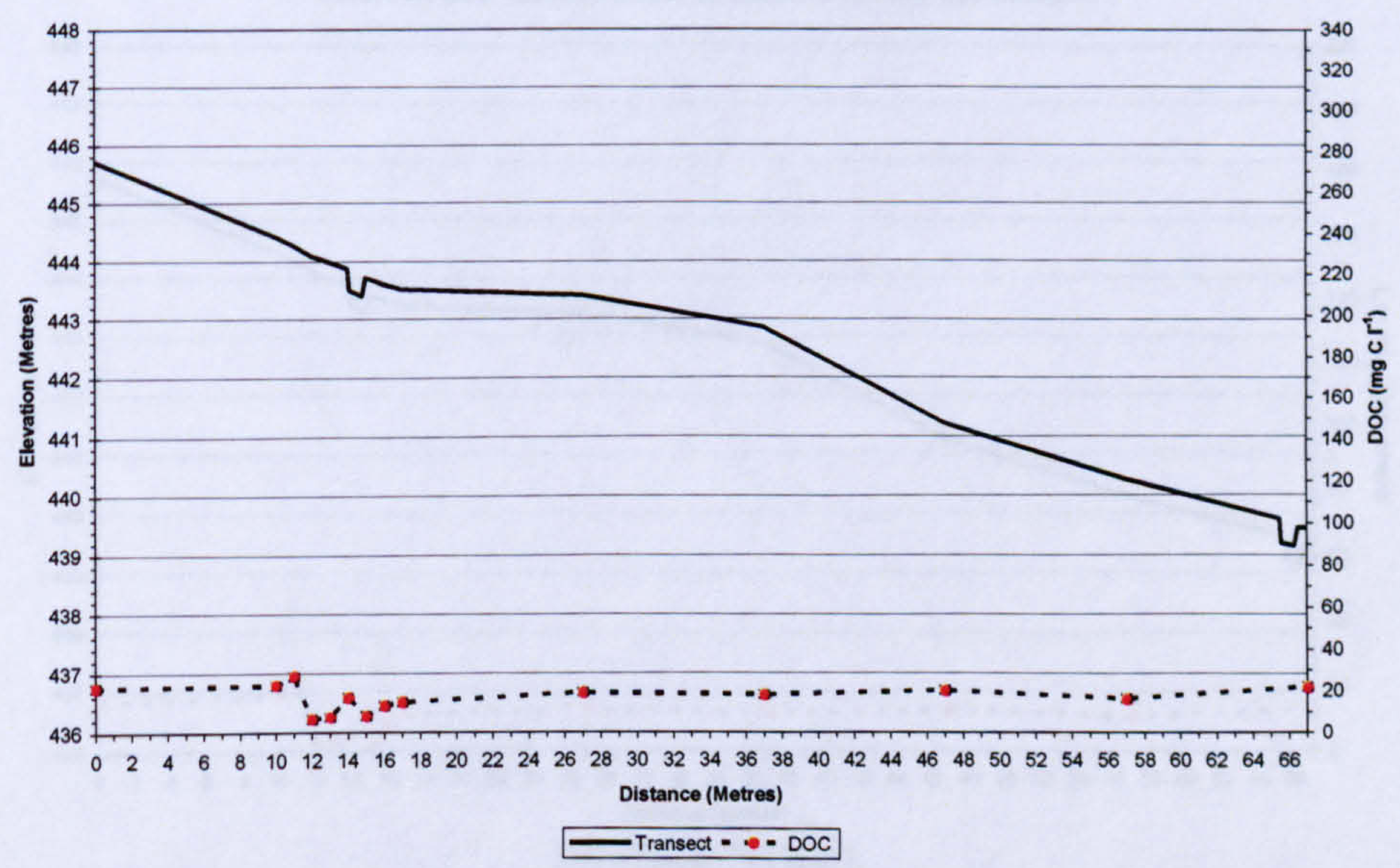


Figure 4.27 How DOC in OLF varies across the blocked transect. Vertical bars represent the SE mean.

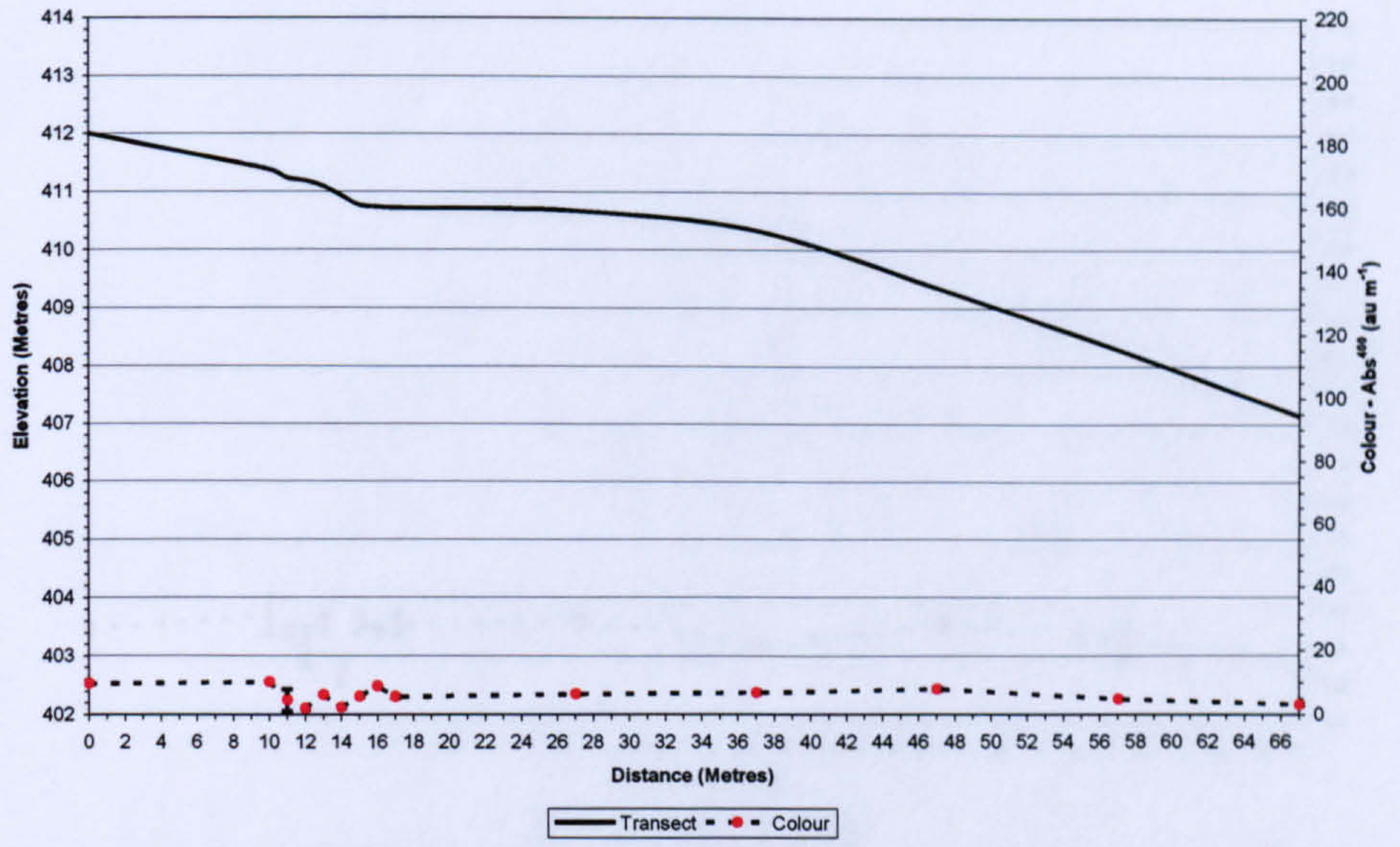


Figure 4.28 How colour (Abs^{400}) in OLF varies across the intact transect. Vertical bars represent the SE mean.

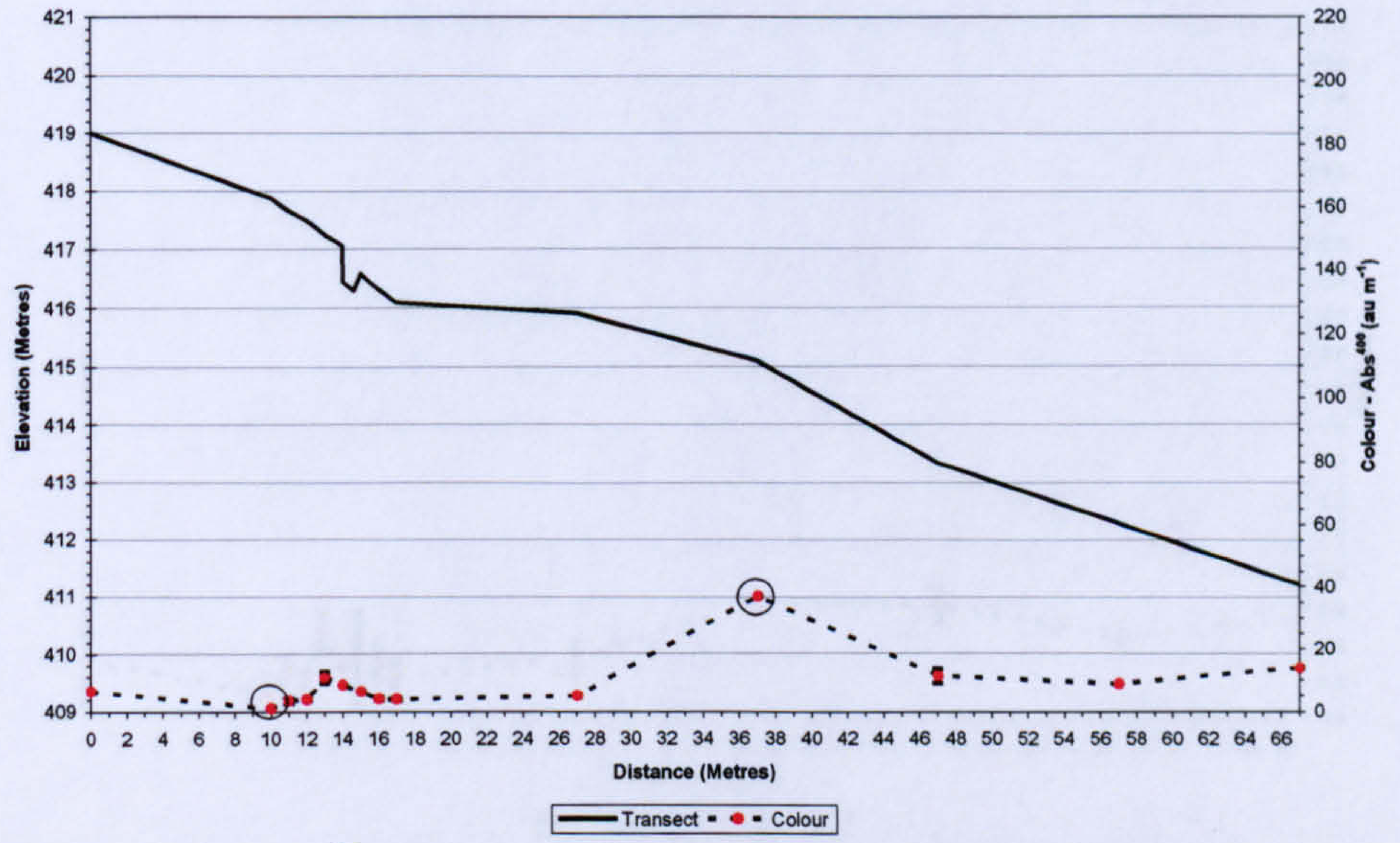


Figure 4.29 How colour (Abs^{400}) in OLF varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

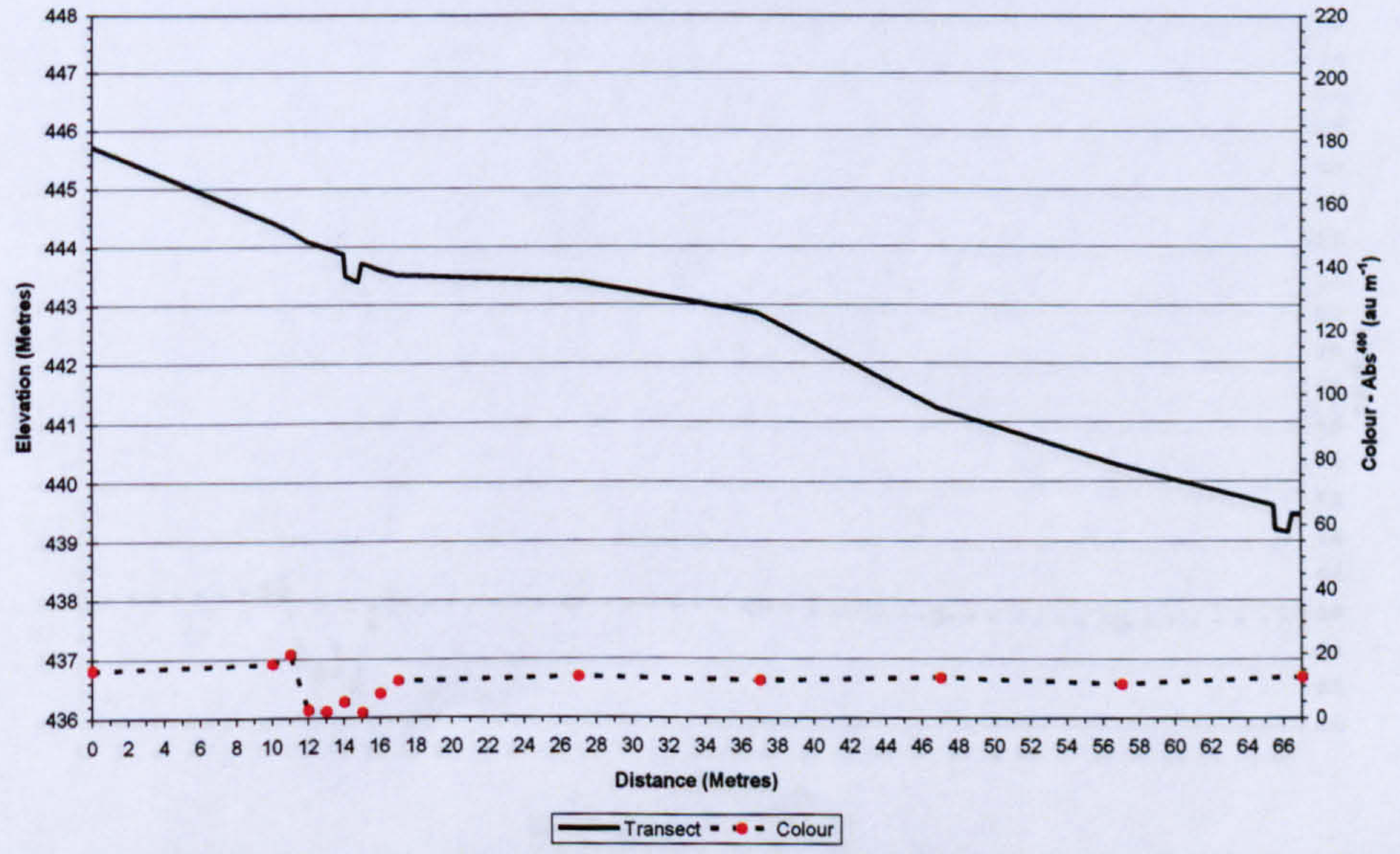


Figure 4.30 How colour (Abs^{400}) in OLF varies across the blocked transect. Vertical bars represent the SE mean.

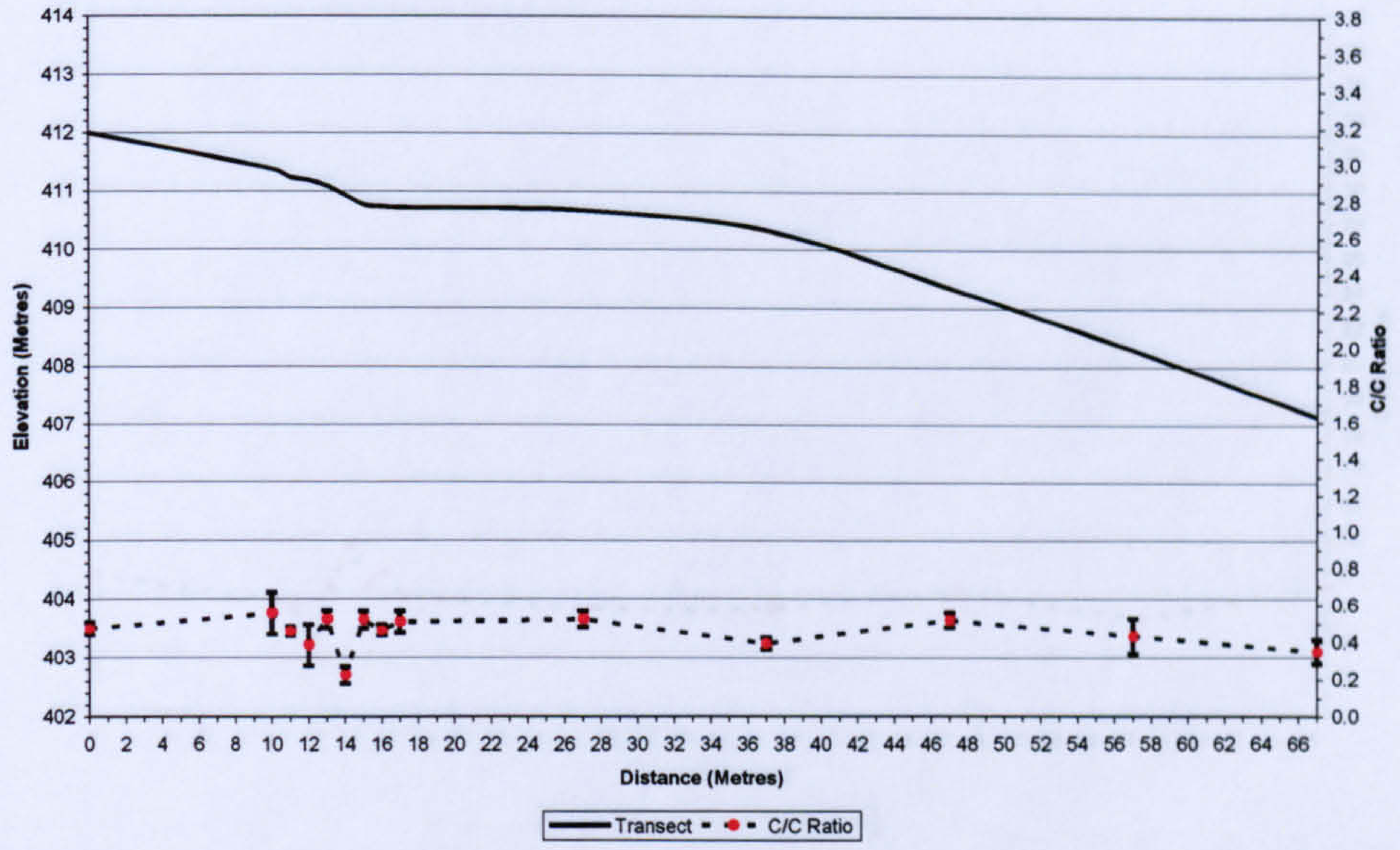


Figure 4.31 How the C/C ratio in OLF varies across the intact transect. Vertical bars represent the SE mean.

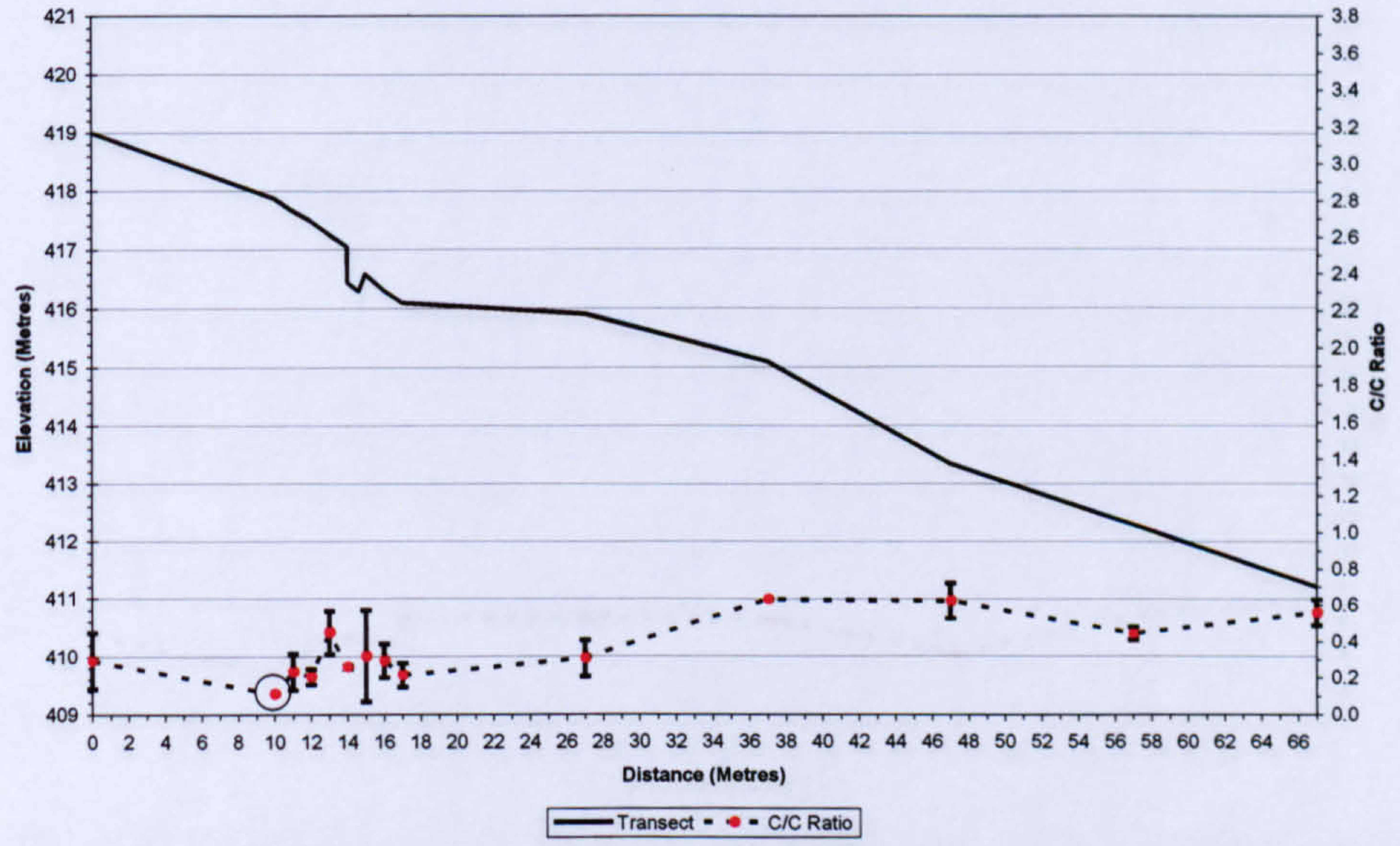


Figure 4.32 How the C/C ratio in OLF varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

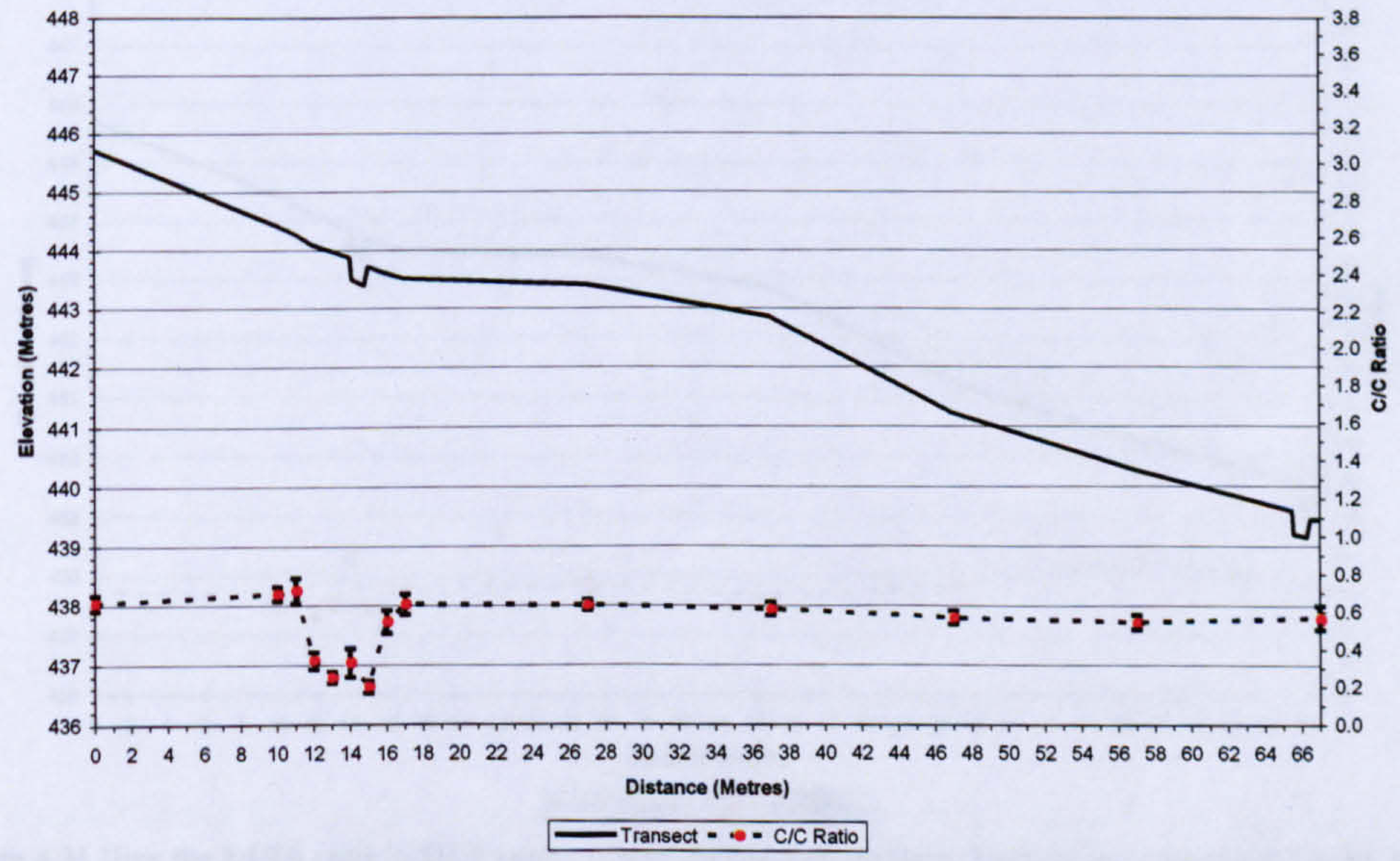


Figure 4.33 How the C/C ratio in OLF varies across the blocked transect. Vertical bars represent the SE mean.

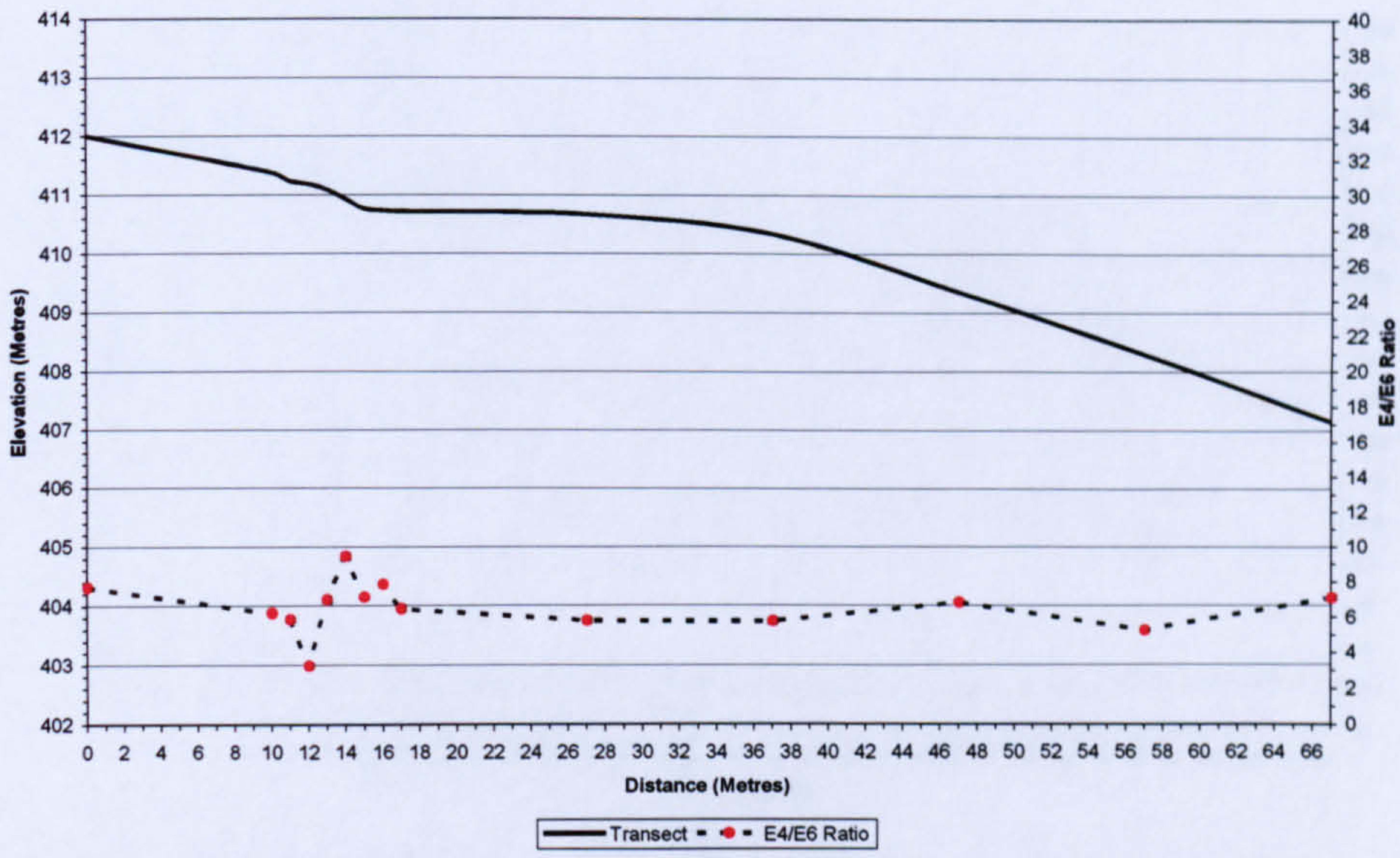


Figure 4.34 How the E4/E6 ratio in OLF varies across the intact transect. Vertical bars represent the SE mean.

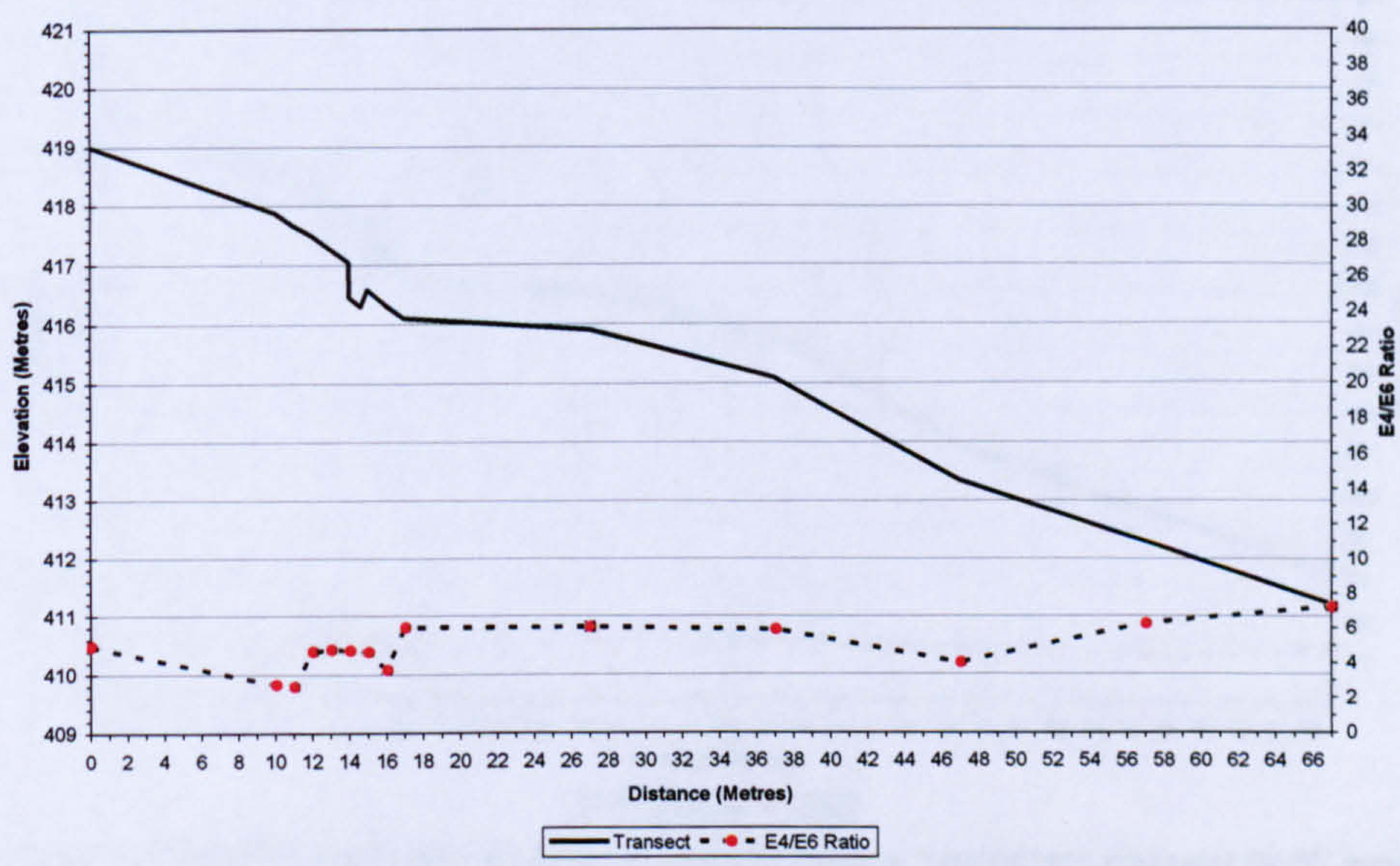


Figure 4.35 How the E4/E6 ratio in OLF varies across the drained transect. Vertical bars represent the SE mean.

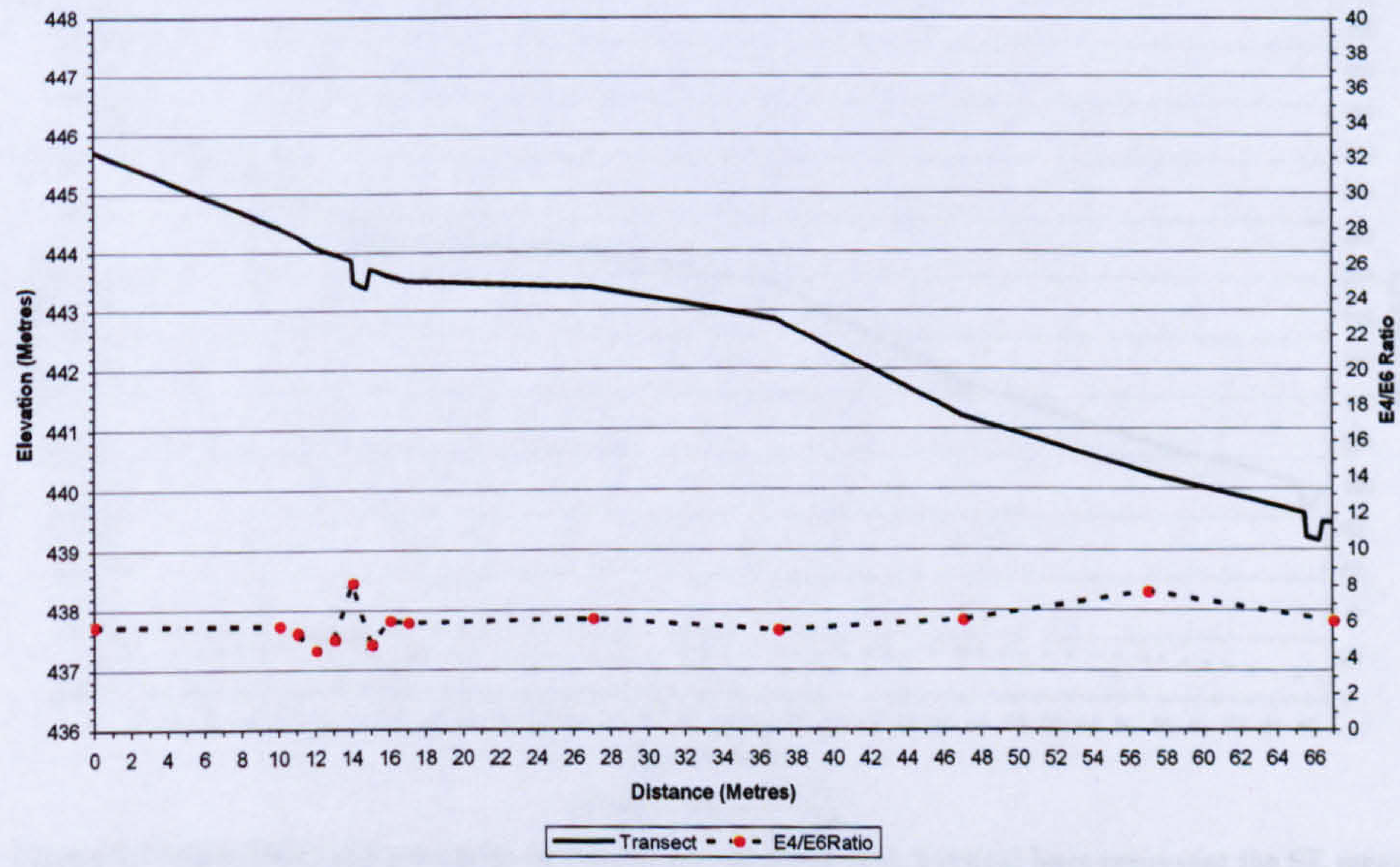


Figure 4.36 How the E4/E6 ratio in OLF varies across the blocked transect. Vertical bars represent the SE mean.

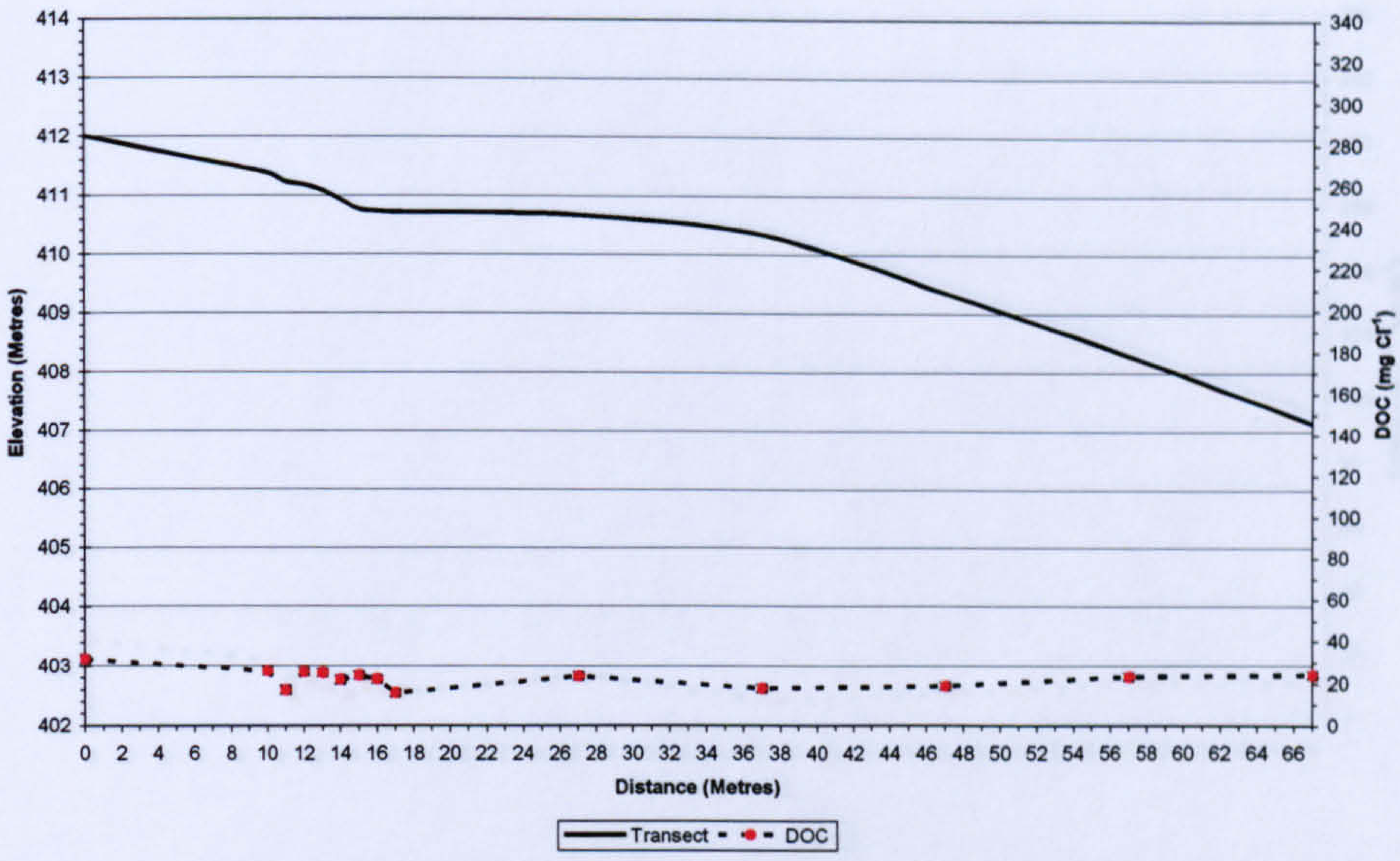


Figure 4.37 How DOC at 5 cm varies across the intact transect. Vertical bars represent the SE mean.

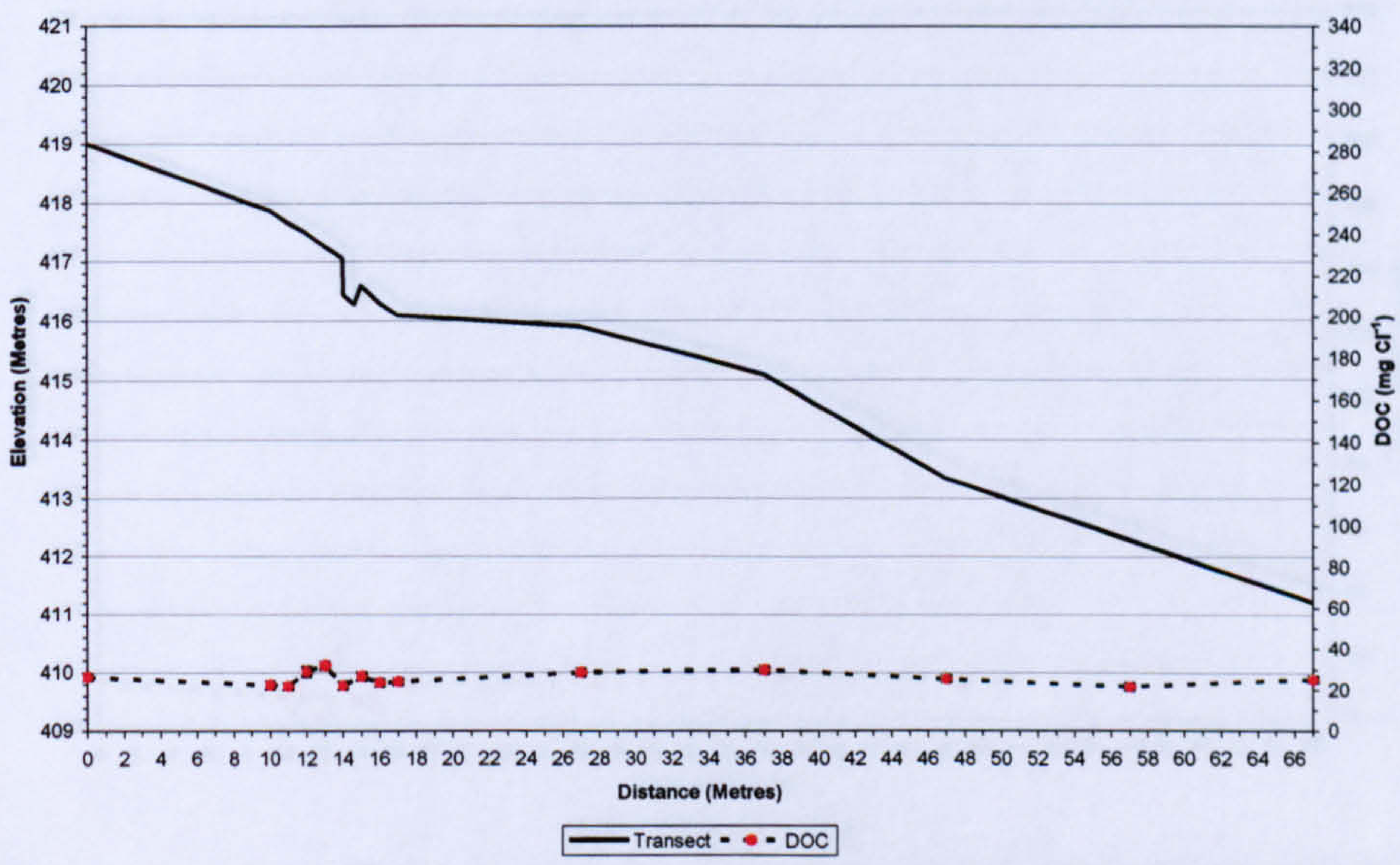


Figure 4.38 How DOC at 5 cm varies across the drained transect. Vertical bars represent the SE mean.

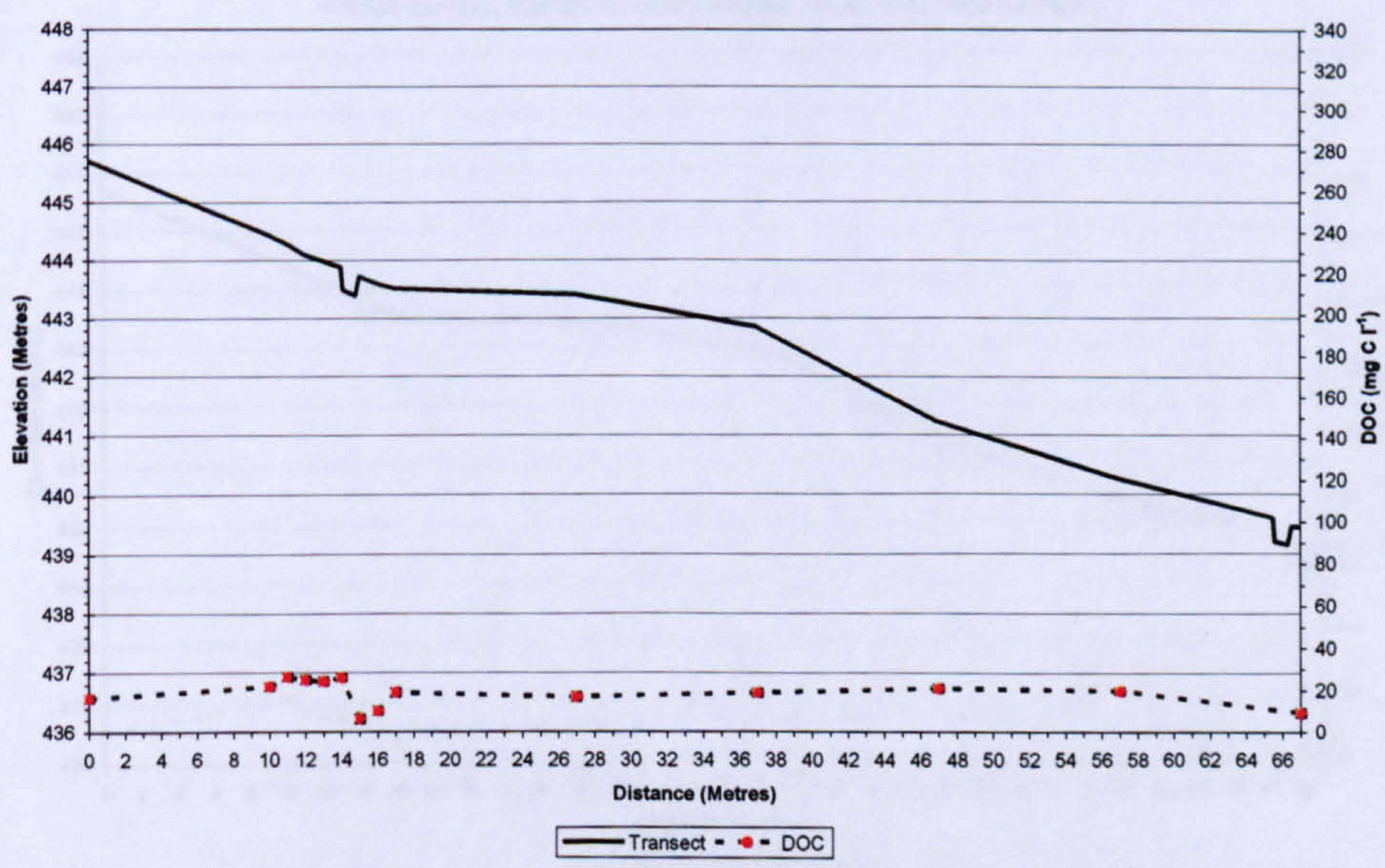


Figure 4.39 How DOC at 5 cm varies across the blocked transect. Vertical bars represent the SE mean.

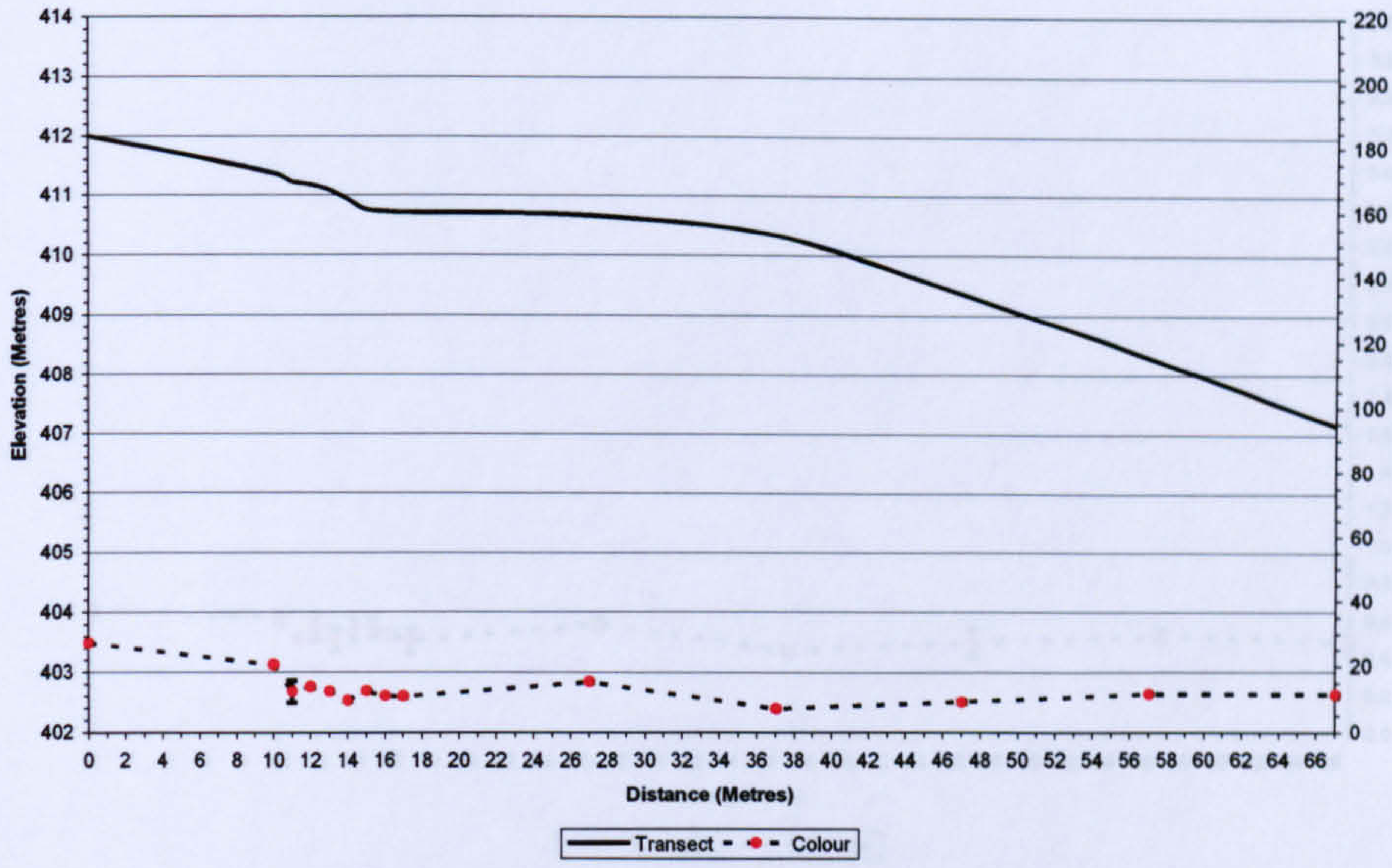


Figure 4.40 How colour (Abs^{400}) at 5 cm varies across the intact transect. Vertical bars represent the SE mean.

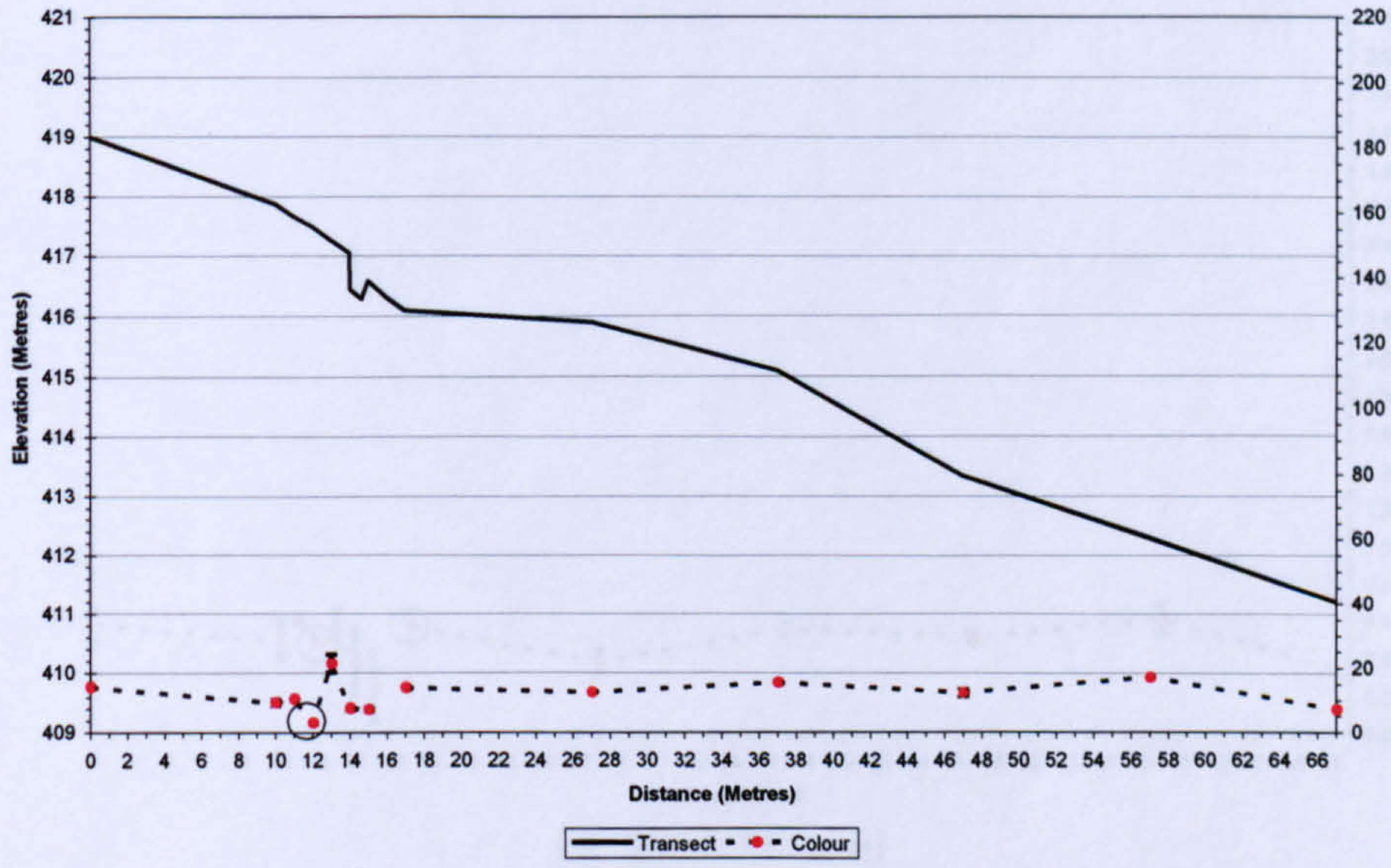


Figure 4.41 How colour (Abs^{400}) at 5 cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

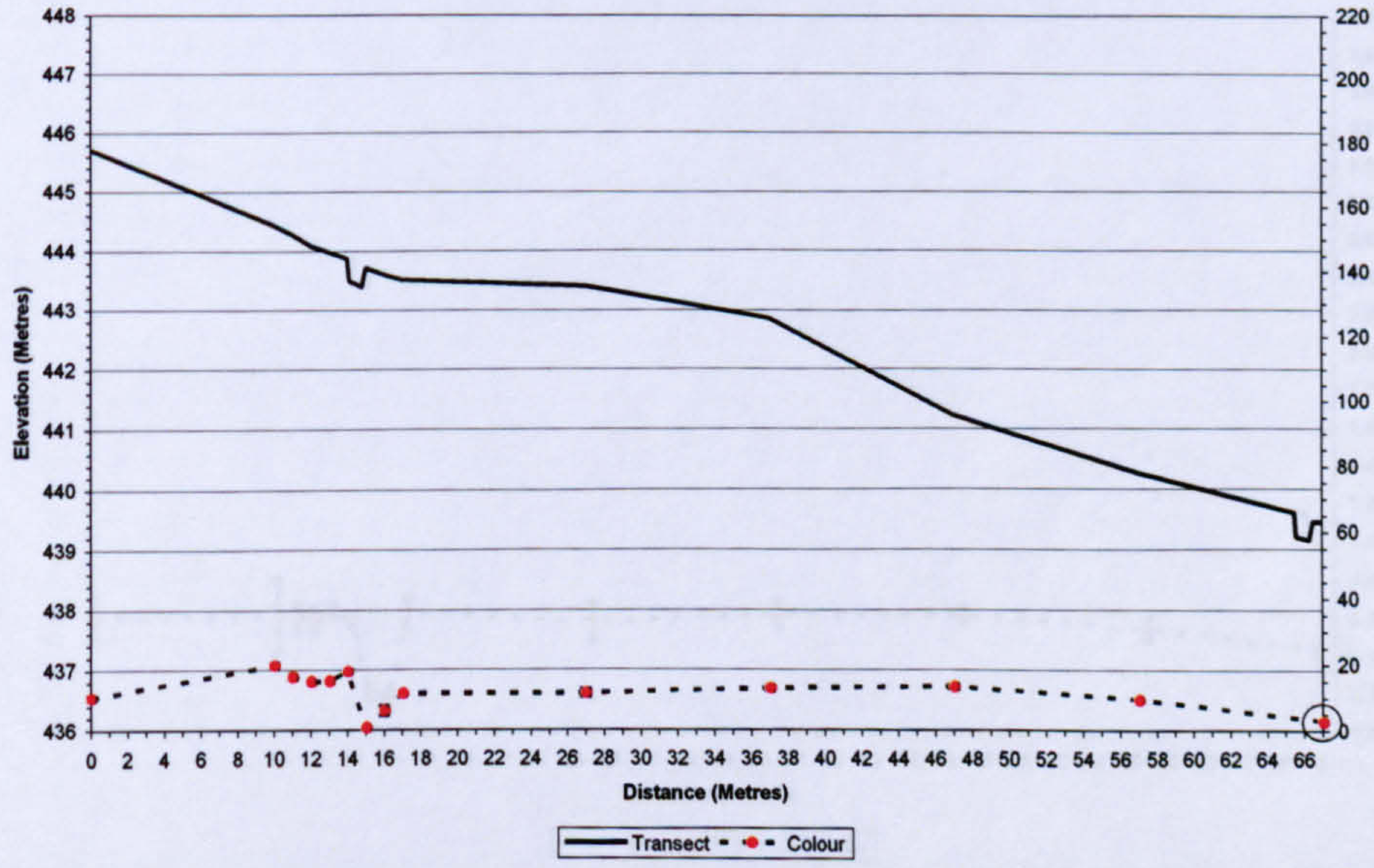


Figure 4.42 How colour (Abs^{400}) at 5 cm varies across the blocked transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

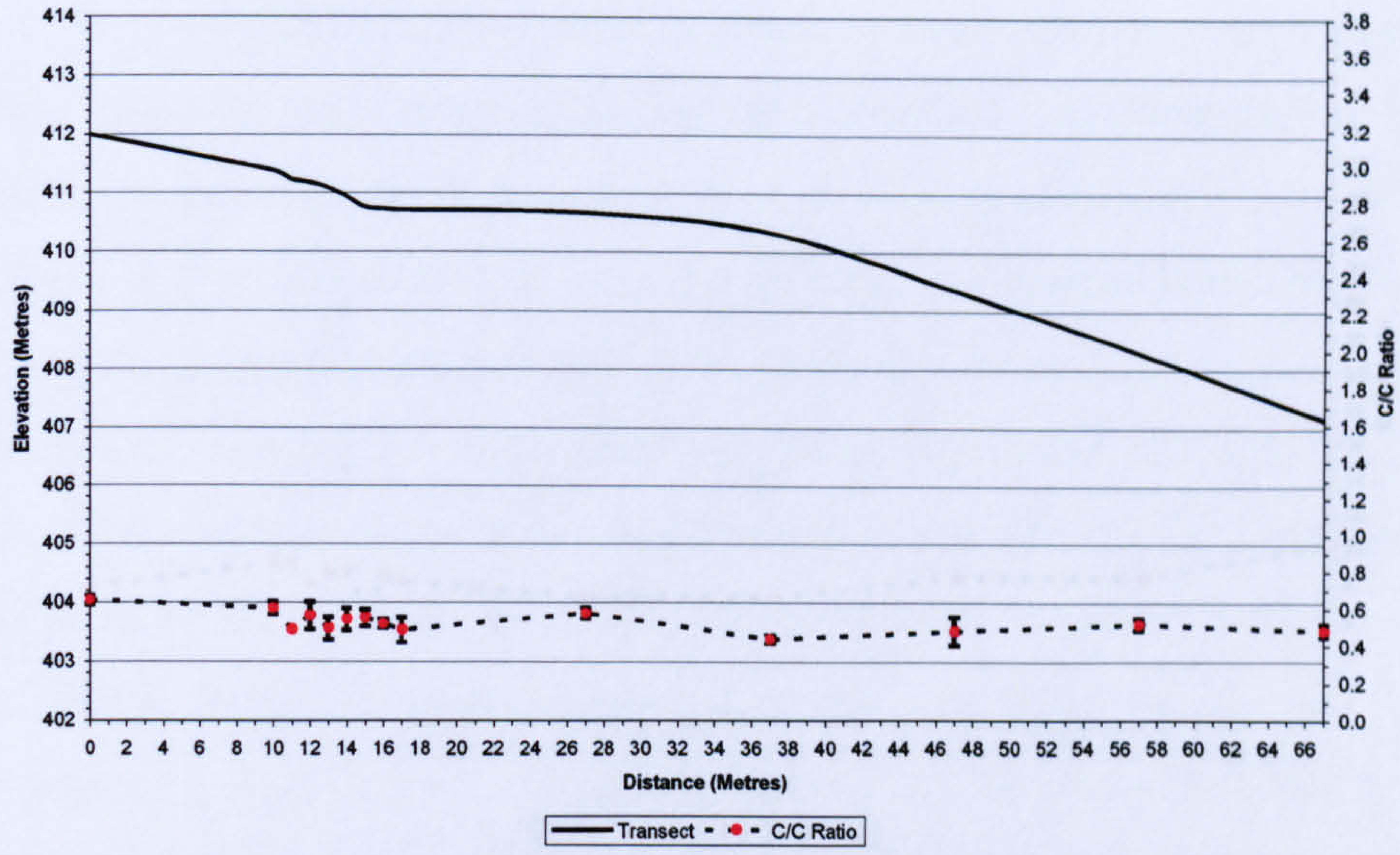


Figure 4.43 How the C/C ratio at 5 cm varies across the intact transect. Vertical bars represent the SE mean.

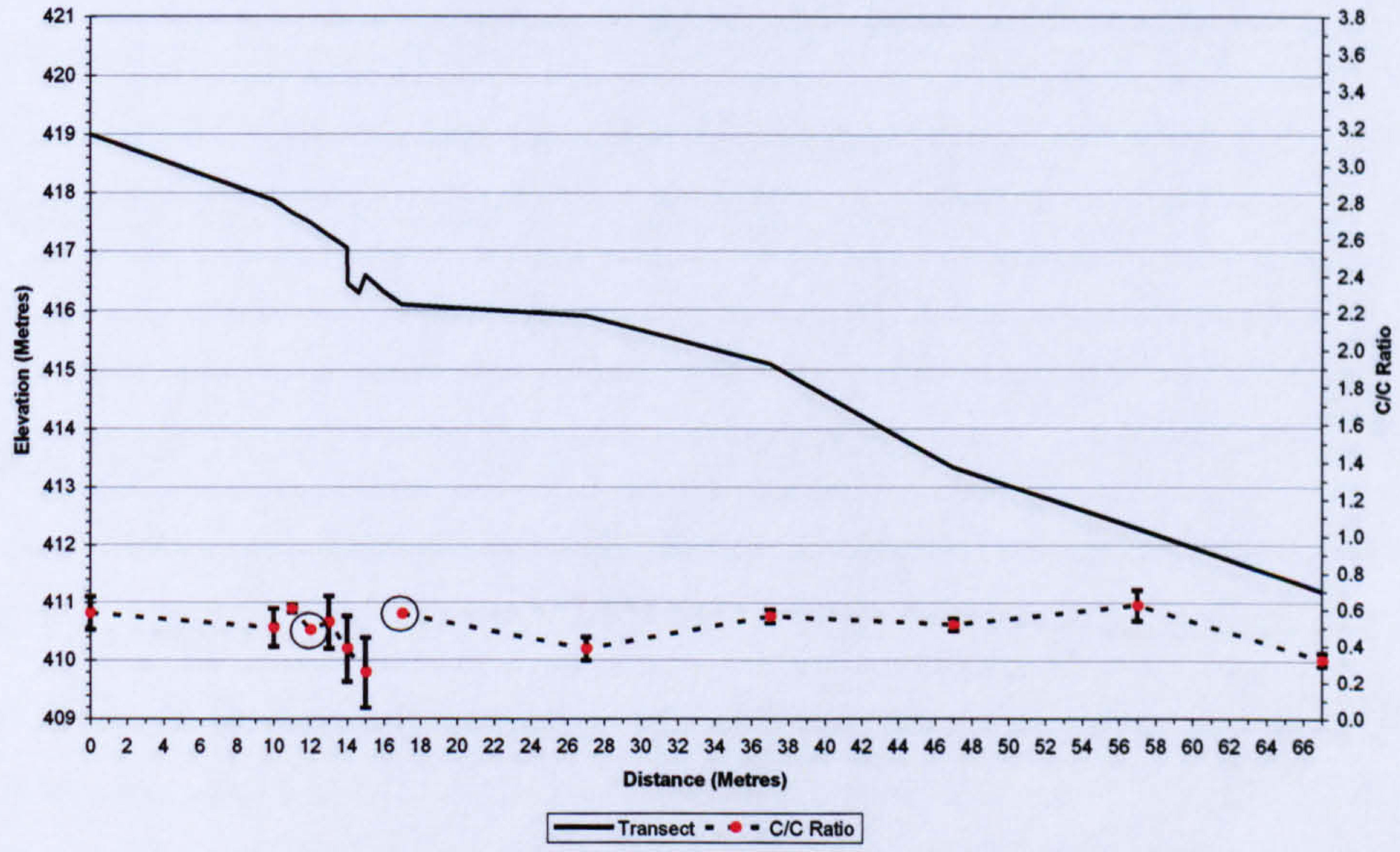


Figure 4.44 How the C/C ratio at 5 cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

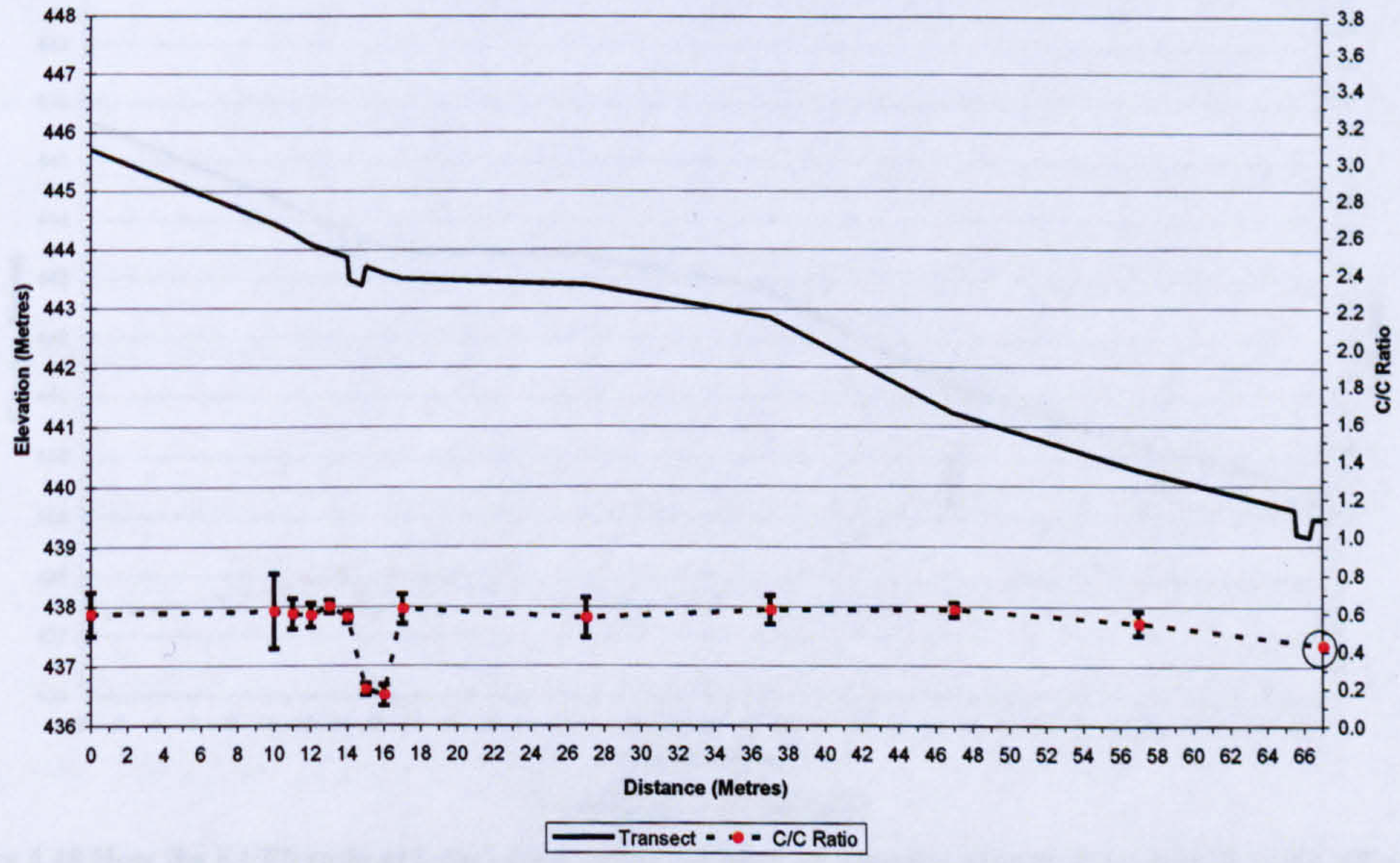


Figure 4.45 How the C/C ratio at 5 cm varies across the blocked transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

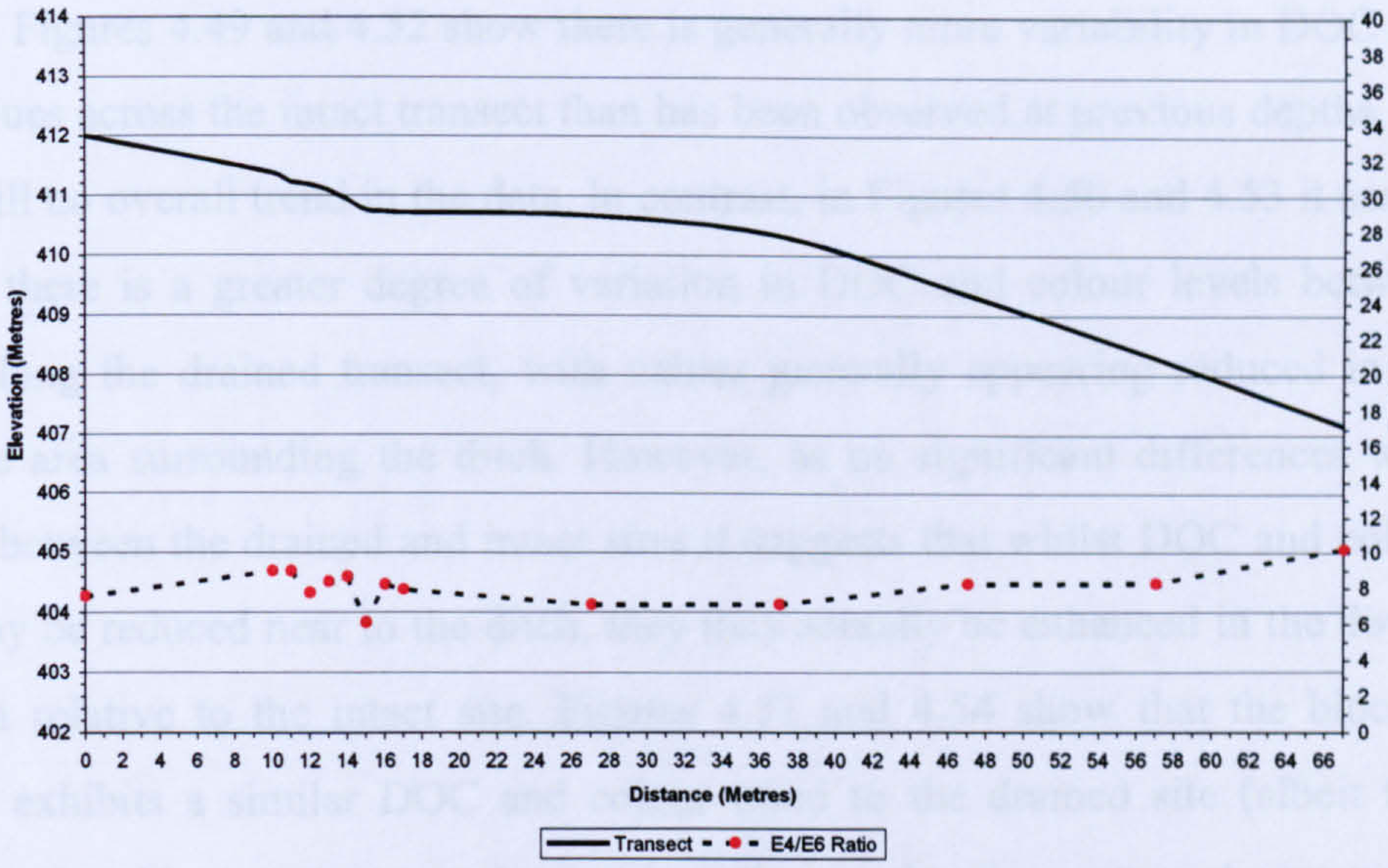


Figure 4.46 How the E4/E6 ratio at 5 cm varies across the intact transect. Vertical bars represent the SE mean.

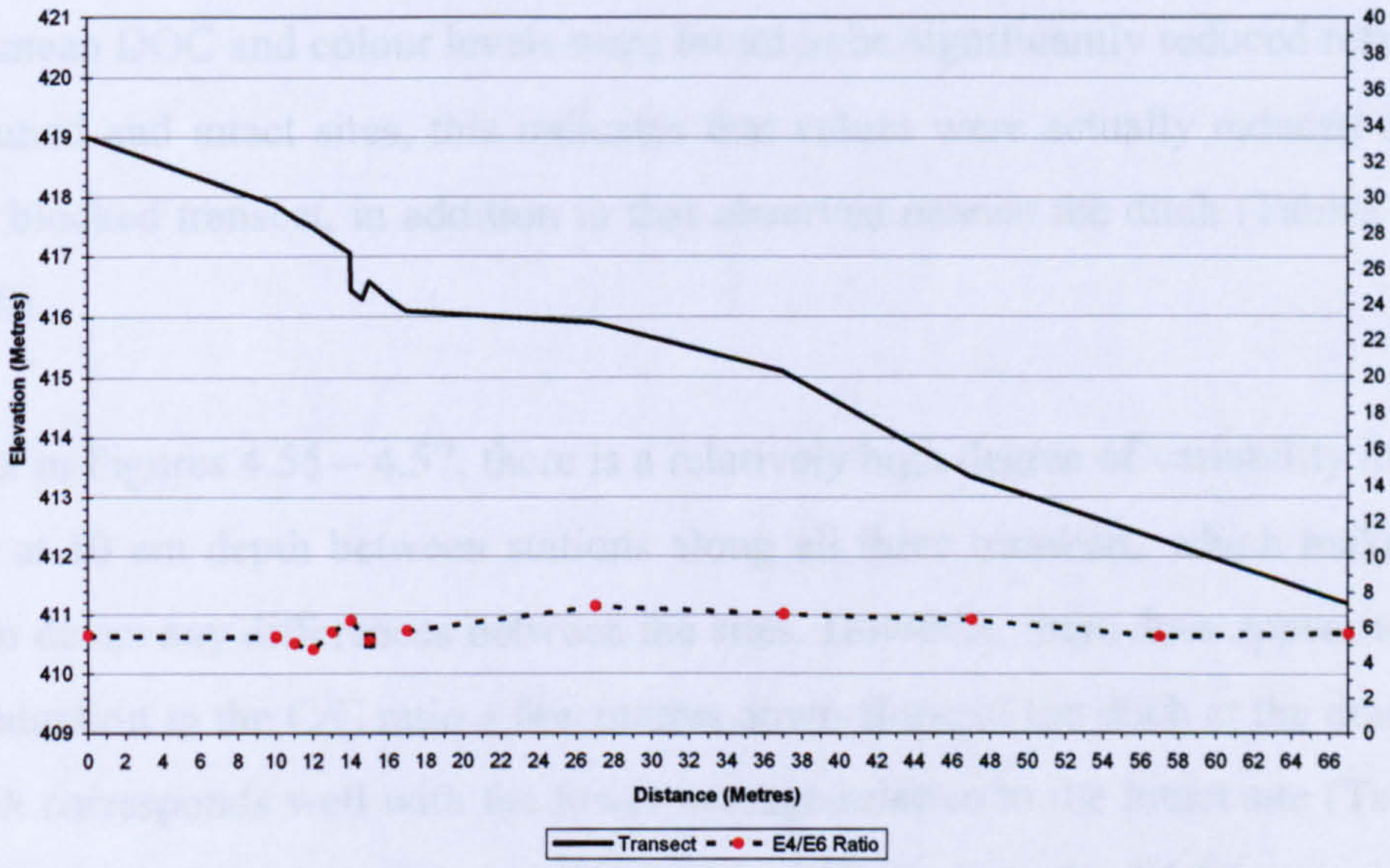


Figure 4.47 How the E4/E6 ratio at 5 cm varies across the drained transect. Vertical bars represent the SE mean.

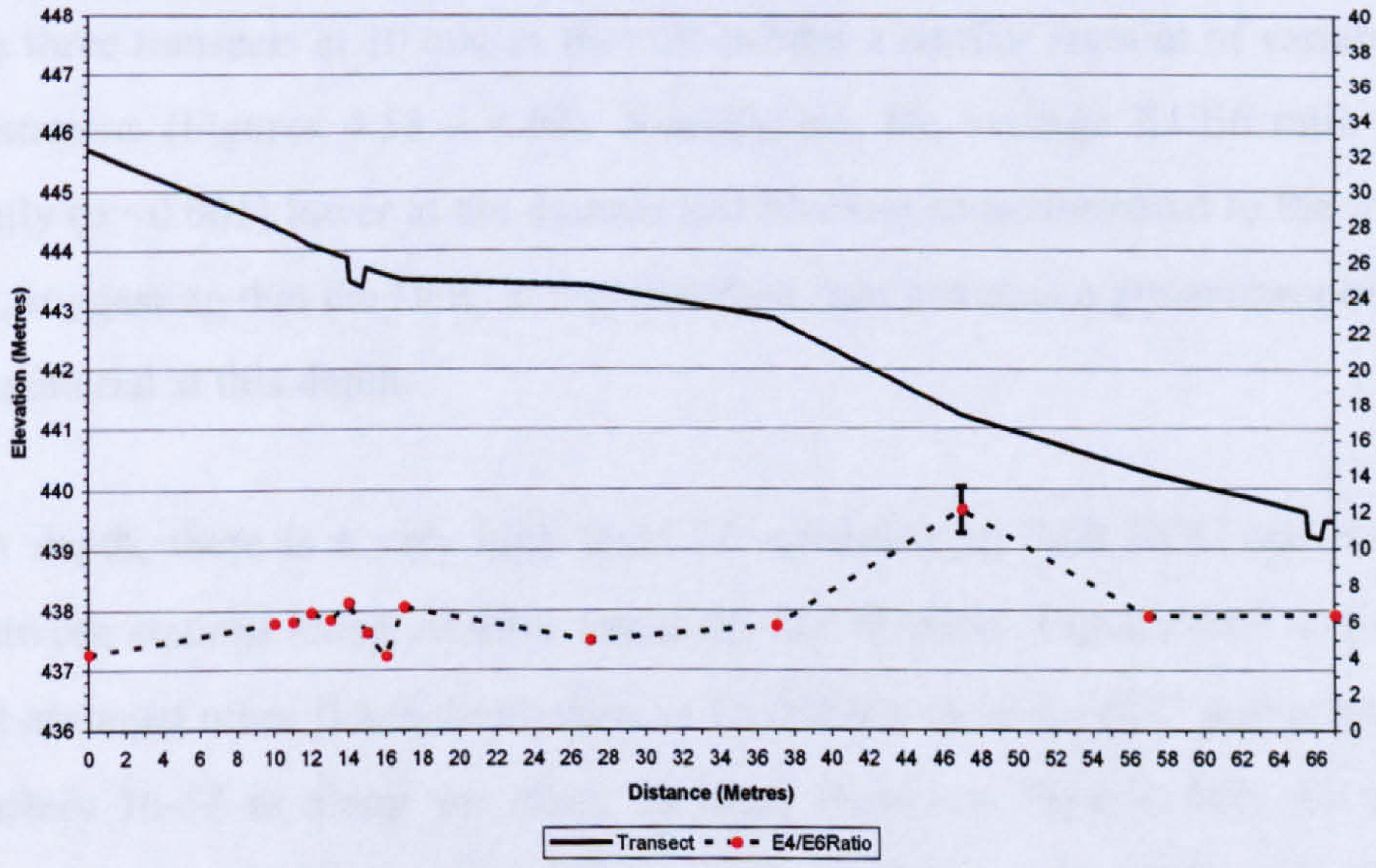


Figure 4.48 How the E4/E6 ratio at 5 cm varies across the blocked transect. Vertical bars represent the SE mean.

At 10 cm, Figures 4.49 and 4.52 show there is generally more variability in DOC and colour values across the intact transect than has been observed at previous depths, but there is still no overall trend in the data. In contrast, in Figures 4.50 and 4.53 it can be seen that there is a greater degree of variation in DOC and colour levels between stations along the drained transect, with values generally appearing reduced in the immediate area surrounding the ditch. However, as no significant differences were observed between the drained and intact sites it suggests that whilst DOC and colour values may be reduced near to the ditch, they may actually be enhanced in the down-slope area relative to the intact site. Figures 4.51 and 4.54 show that the blocked treatment exhibits a similar DOC and colour trend to the drained site (albeit to a lesser extent), with an apparent reduction in values in the few metres closest to the ditch. As mean DOC and colour levels were found to be significantly reduced relative to the drained and intact sites, this indicates that values were actually reduced over the entire blocked transect, in addition to that observed nearest the ditch (Tables 4.6, 4.7 & 4.10).

As evident in Figures 4.55 – 4.57, there is a relatively high degree of variability in the C/C ratio at 10 cm depth between stations along all three transects, which makes it difficult to detect any differences between the sites. However, there does appear to be a slight reduction in the C/C ratio a few metres down-slope of the ditch at the drained site, which corresponds well with the lower average relative to the intact site (Tables 4.8 & 4.10). In addition, there is no discernable difference in the E4/E6 ratio trend across the three transects at 10 cm, as they all exhibit a similar amount of variability between stations (Figures 4.58 – 4.60). Nonetheless, the average E4/E6 ratio was significantly (p <0.001) lower at the drained and blocked sites compared to the intact treatment, suggesting that the DOC at the disturbed sites contains a greater proportion of humic material at this depth.

At 20 cm depth, there is a very high level of variability in both DOC and colour values between stations along all three transects. For example, Figures 4.61 and 4.64 show that amongst other fluctuations there is an definite peak in DOC and colour at approximately 16-18 m along the intact transect. However, Figures 4.62 and 4.65 show that along the drained transect there appears to be an even higher degree of variability, with DOC and colour values visibly enhanced at either side of the ditch,

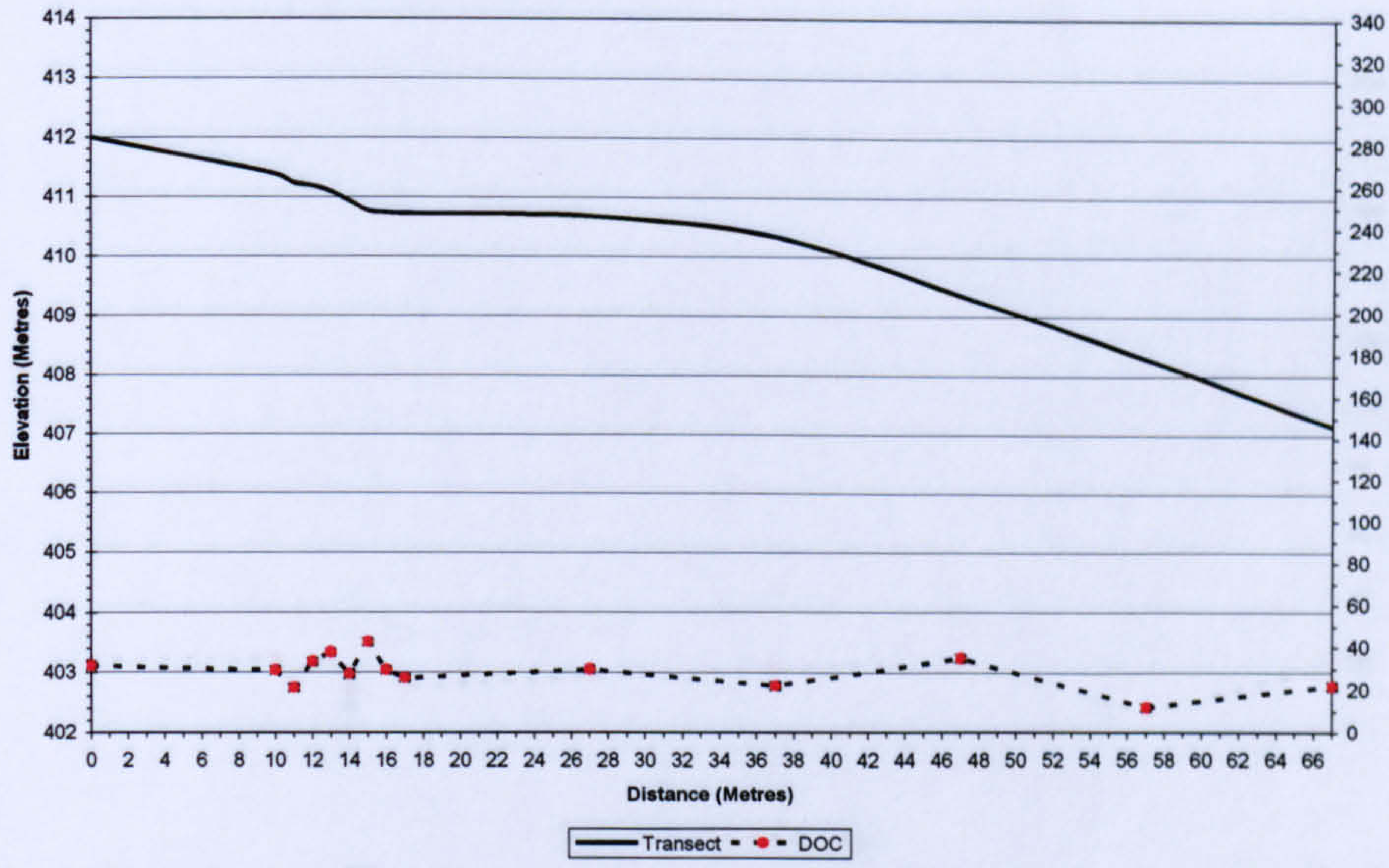


Figure 4.49 How DOC at 10 cm varies across the intact transect. Vertical bars represent the SE mean.

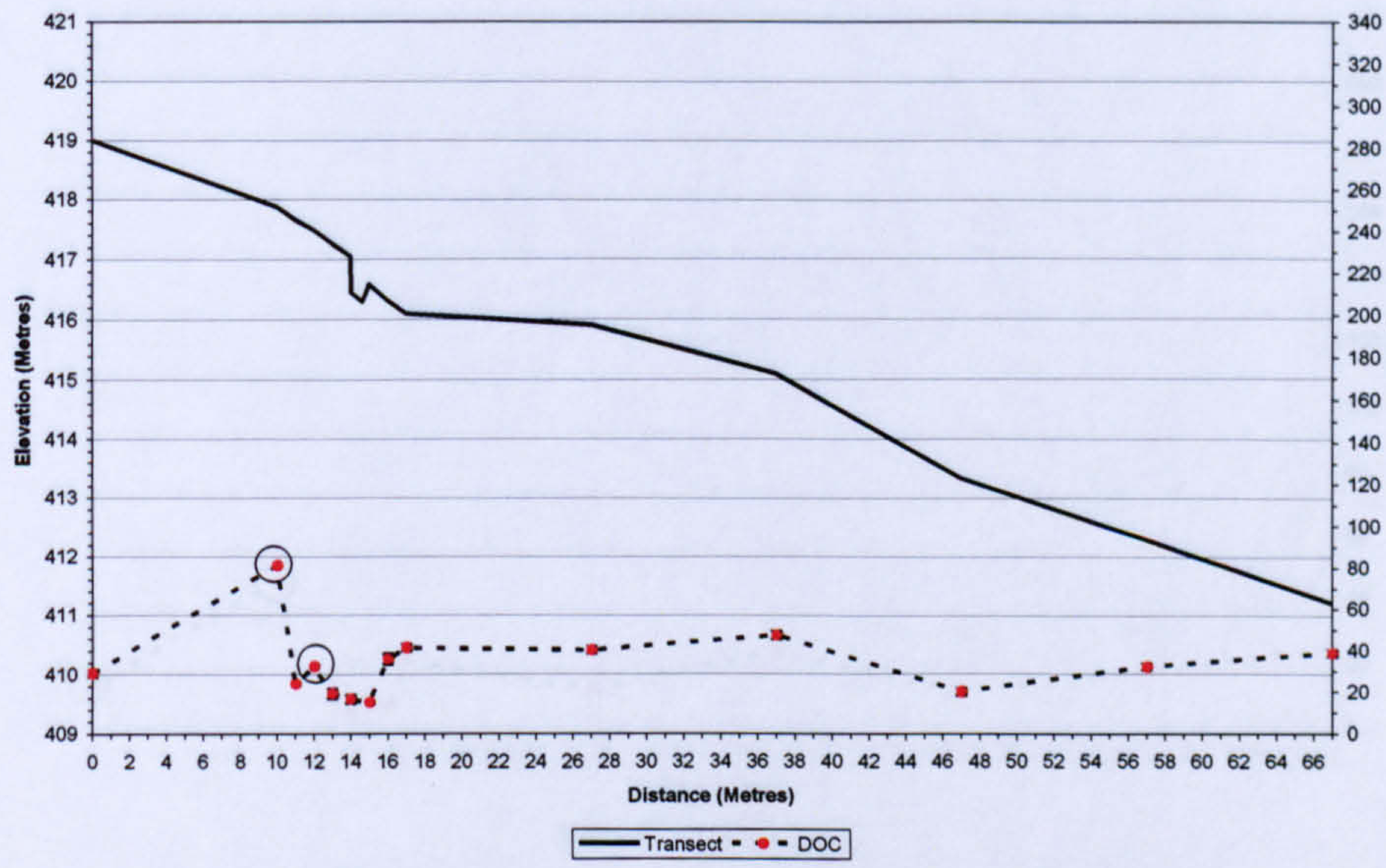


Figure 4.50 How DOC at 10 cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

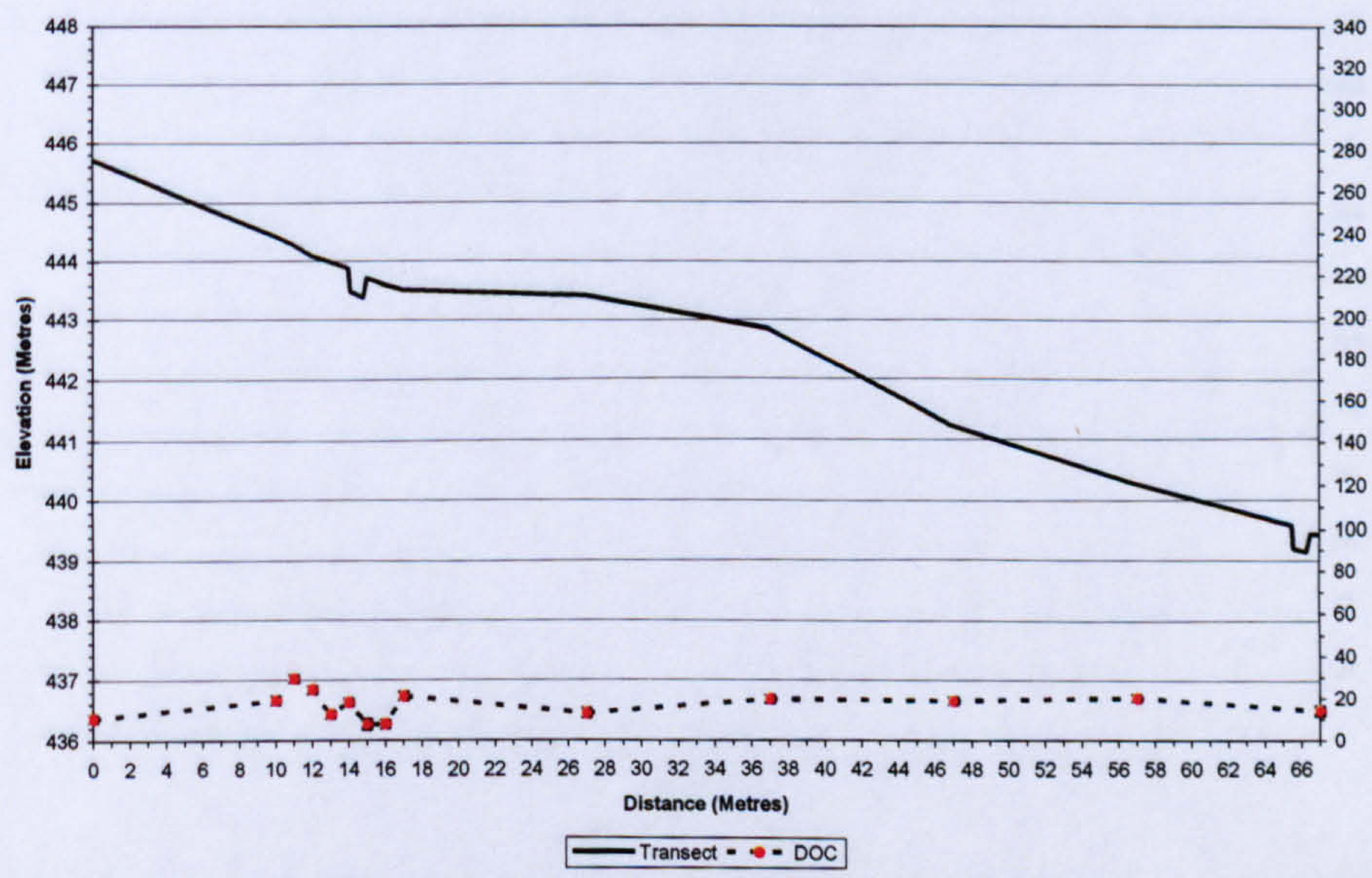


Figure 4.51 How DOC at 10 cm varies across the blocked transect. Vertical bars represent the SE mean.

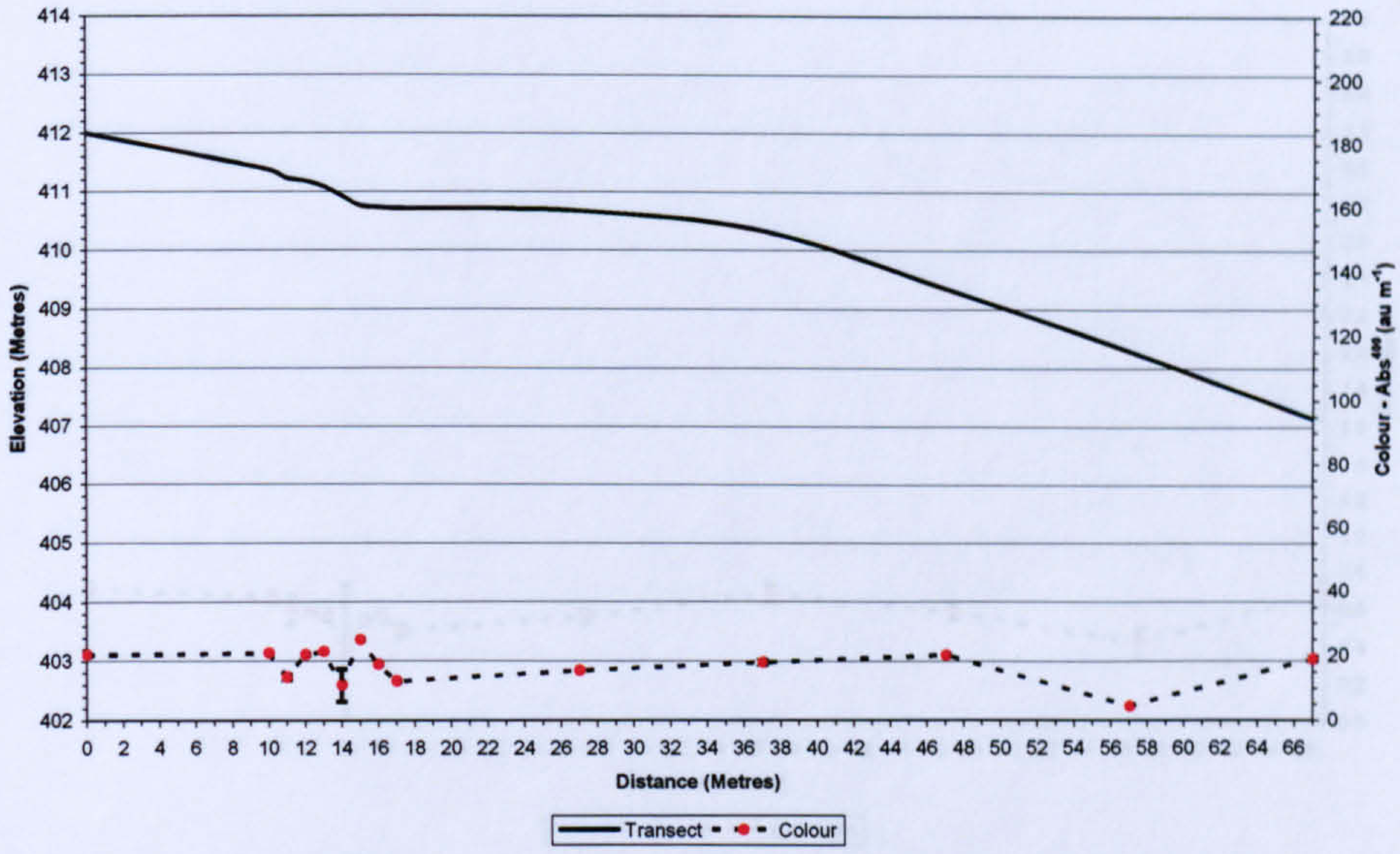


Figure 4.52 How colour (Abs^{400}) at 10 cm varies across the intact transect. Vertical bars represent the SE mean.

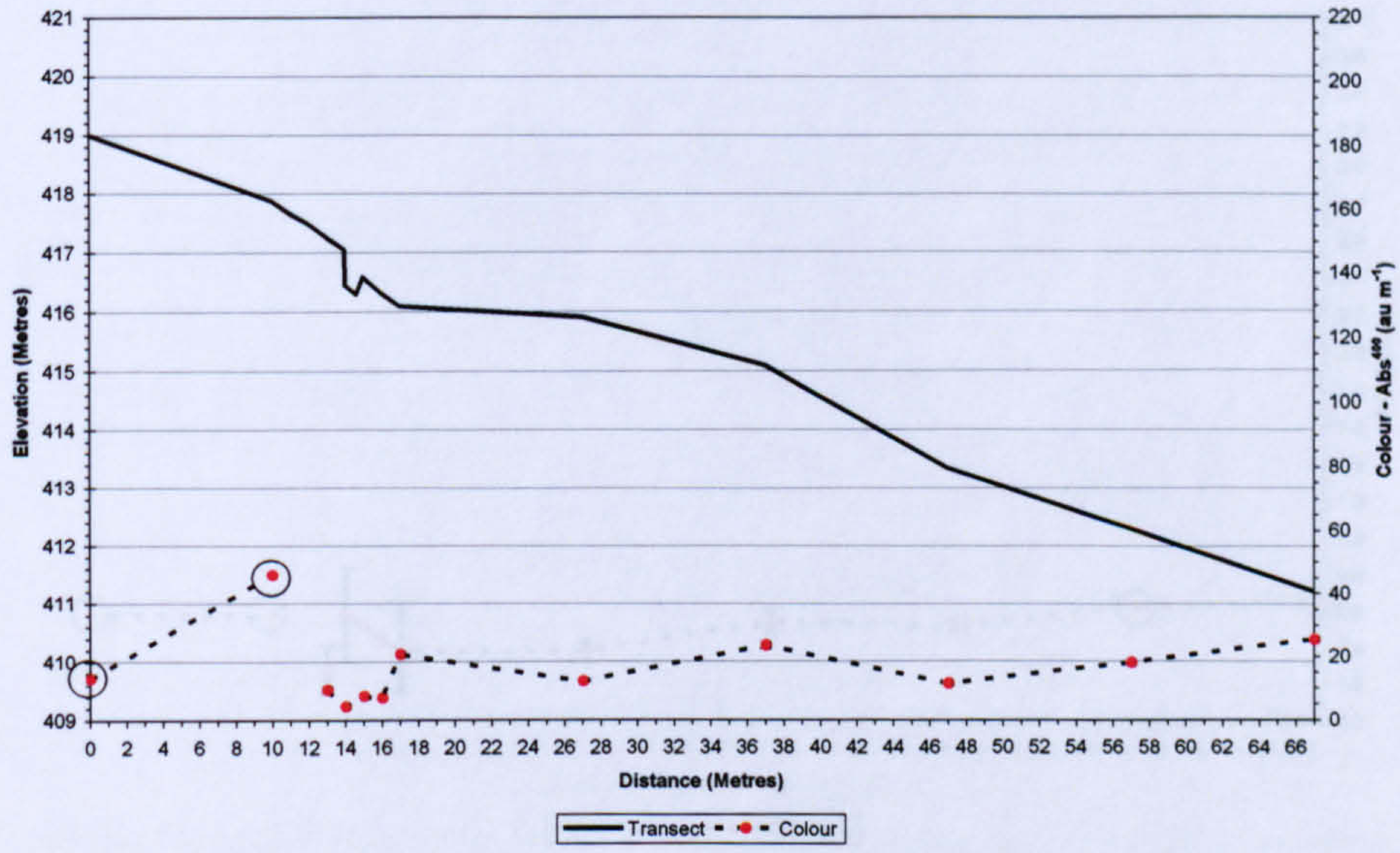


Figure 4.53 How colour (Abs^{400}) at 10 cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

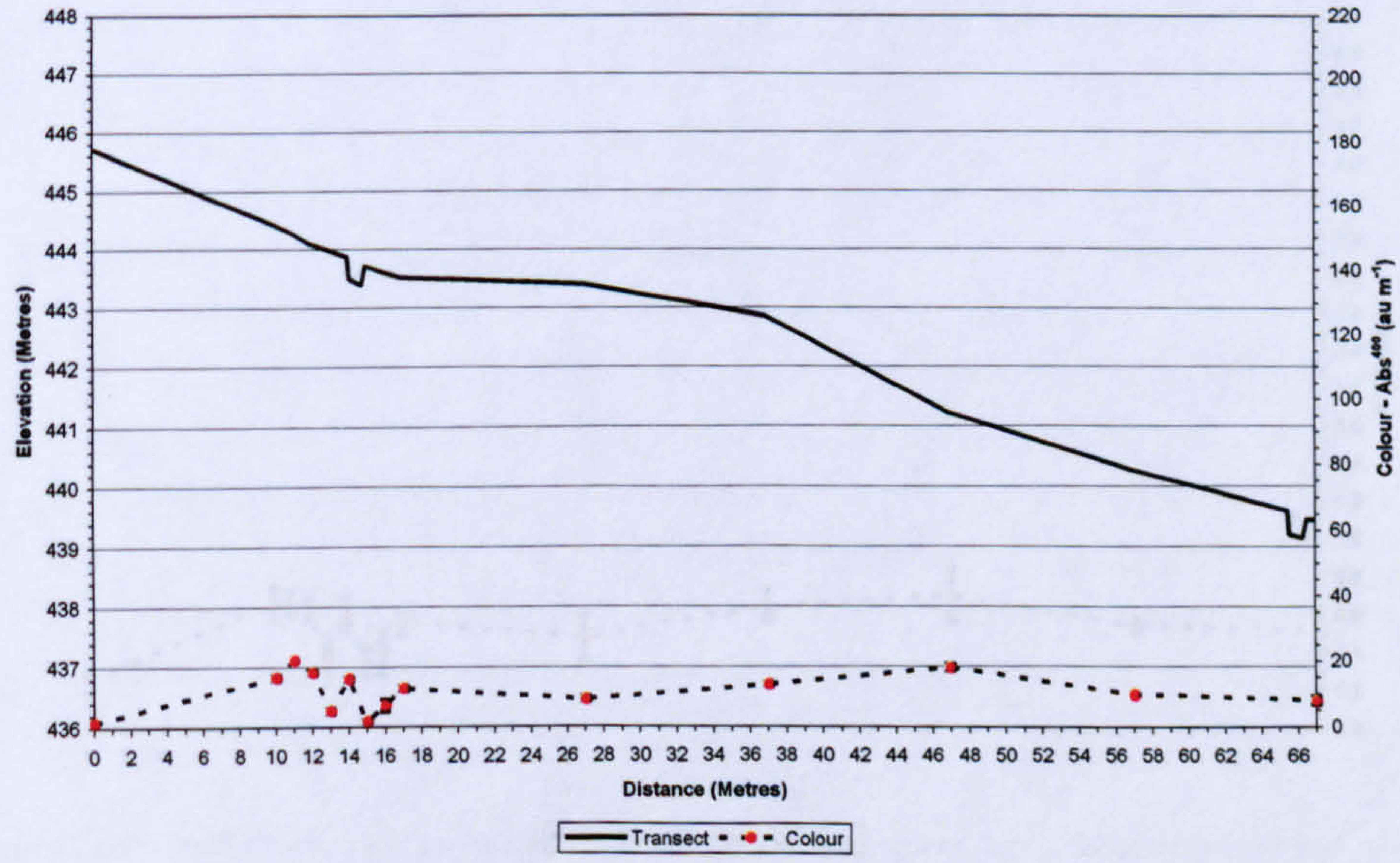


Figure 4.54 How colour (Abs^{400}) at 10 cm varies across the blocked transect. Vertical bars represent the SE mean.

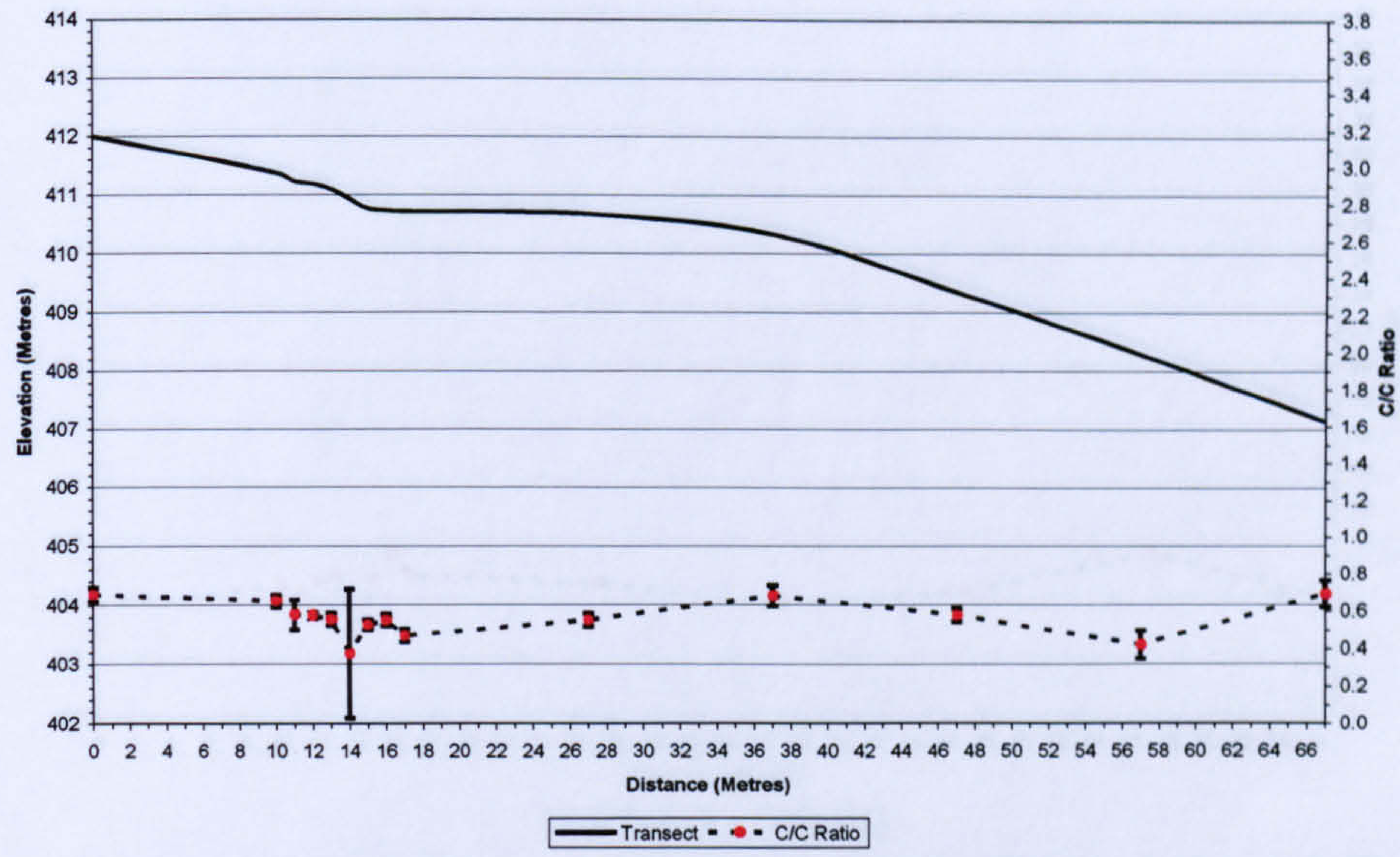


Figure 4.55 How the C/C ratio at 10 cm varies across the intact transect. Vertical bars represent the SE mean.

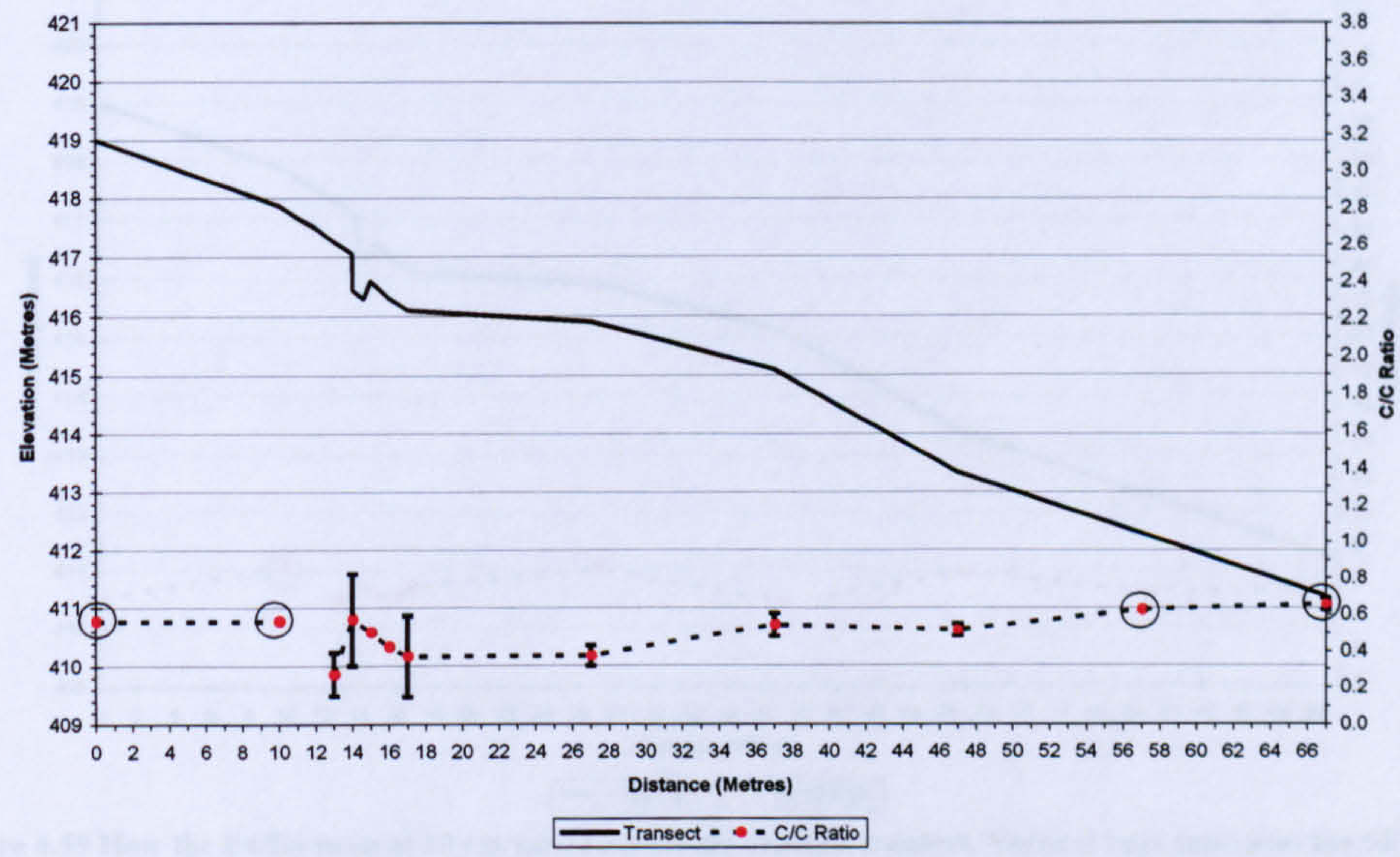


Figure 4.56 How the C/C ratio at 10 cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

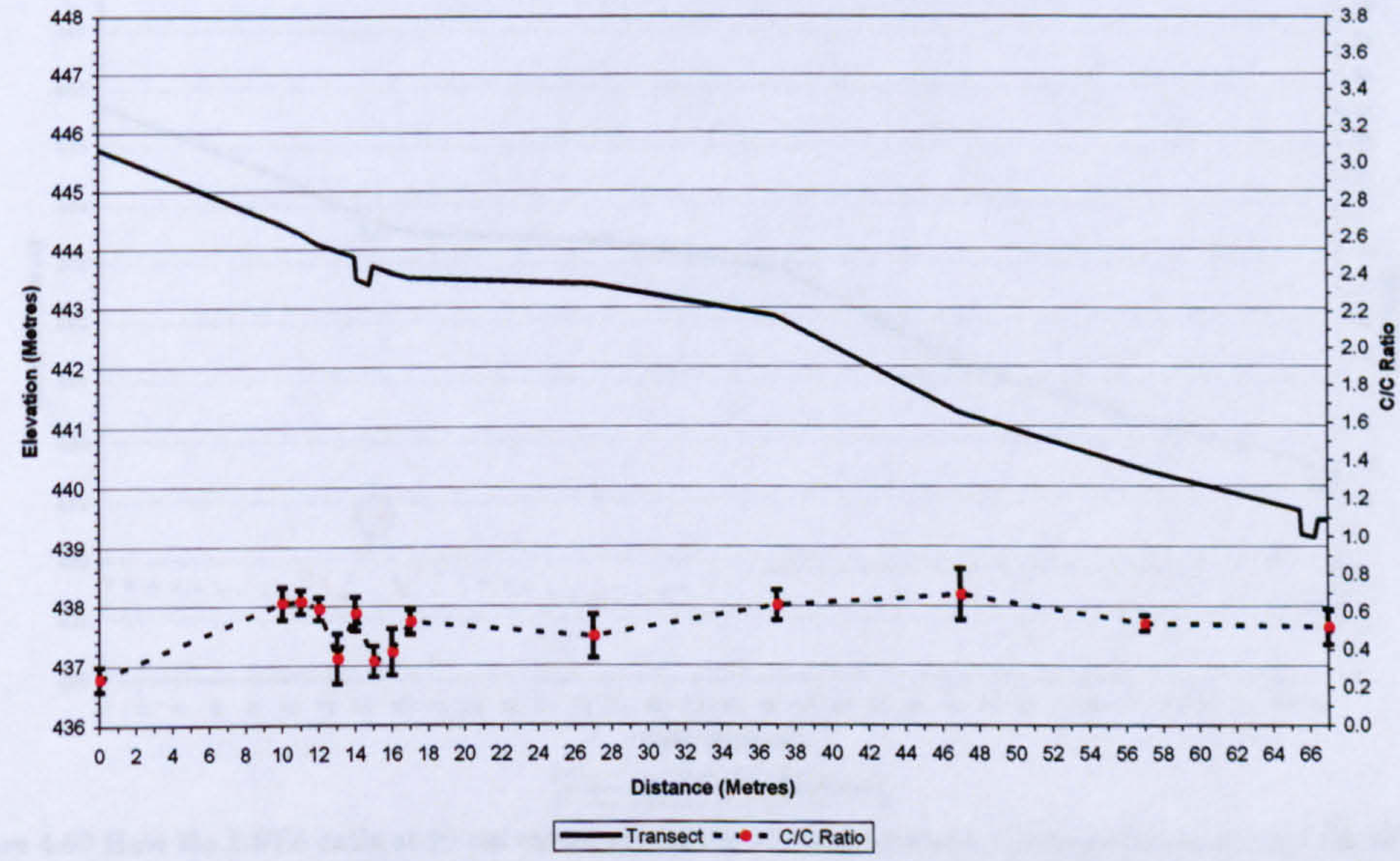


Figure 4.57 How the C/C ratio at 10 cm varies across the blocked transect. Vertical bars represent the SE mean.

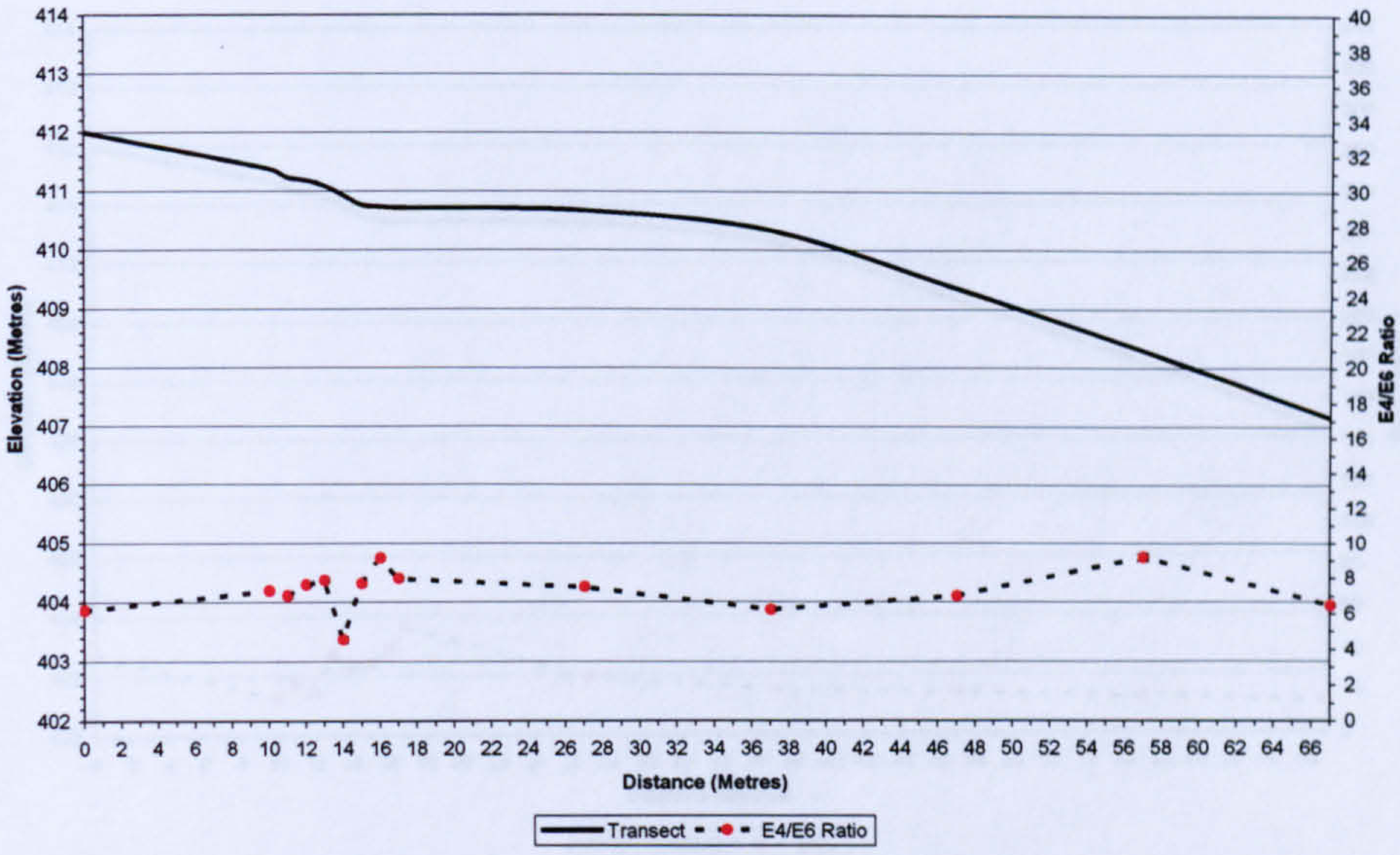


Figure 4.58 How the E4/E6 ratio at 10 cm varies across the intact transect. Vertical bars represent the SE mean.

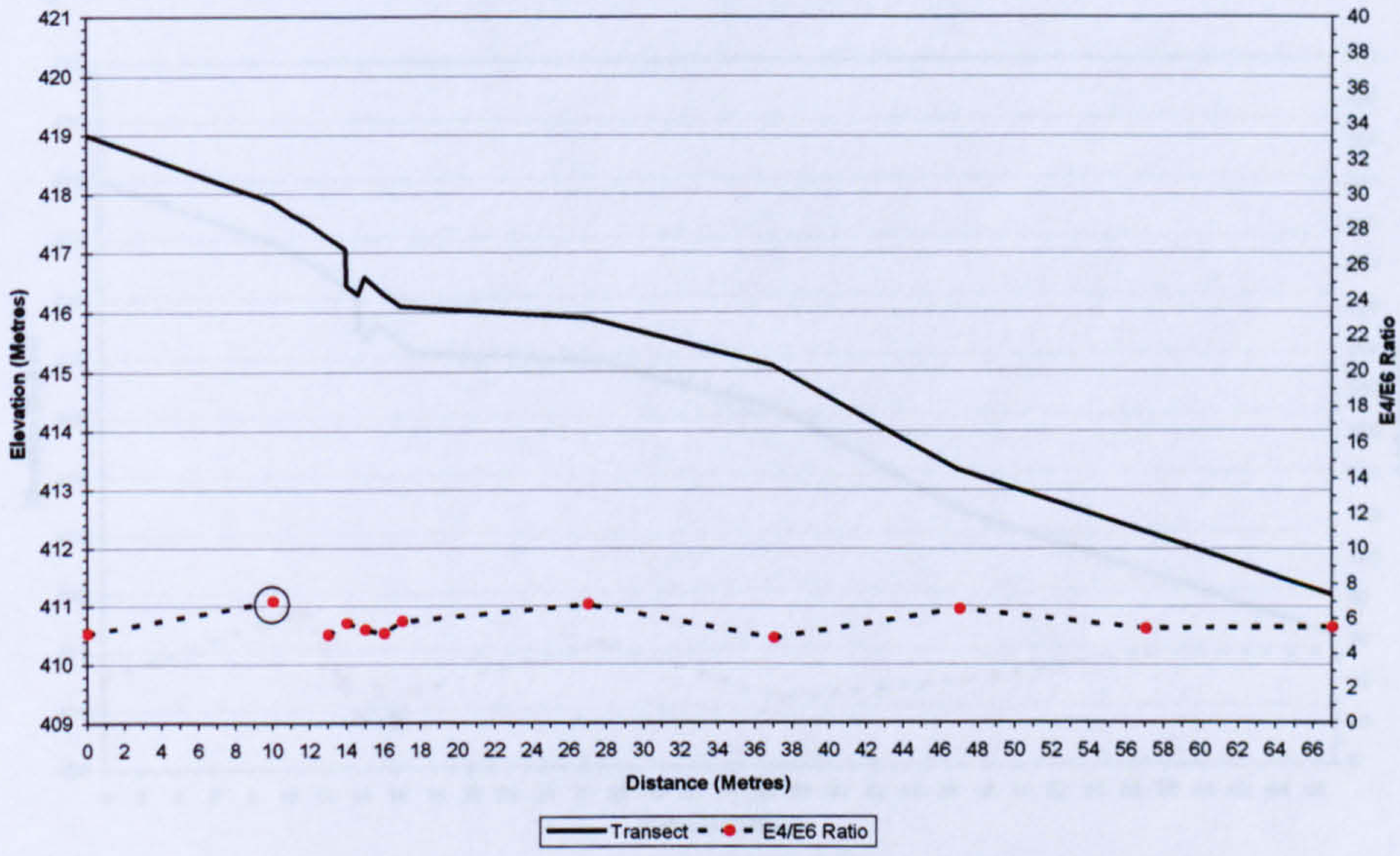


Figure 4.59 How the E4/E6 ratio at 10 cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

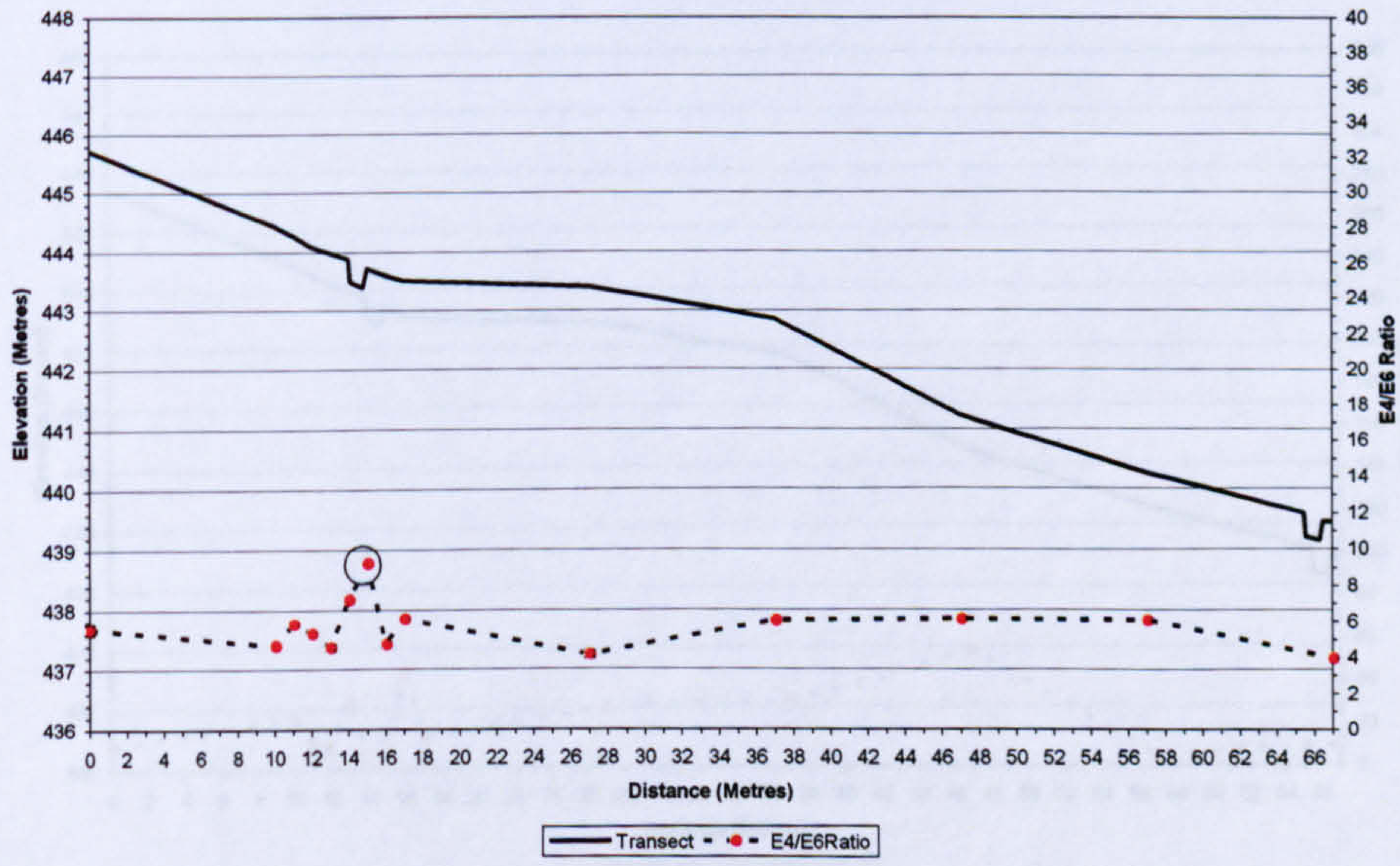


Figure 4.60 How the E4/E6 ratio at 10 cm varies across the blocked transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

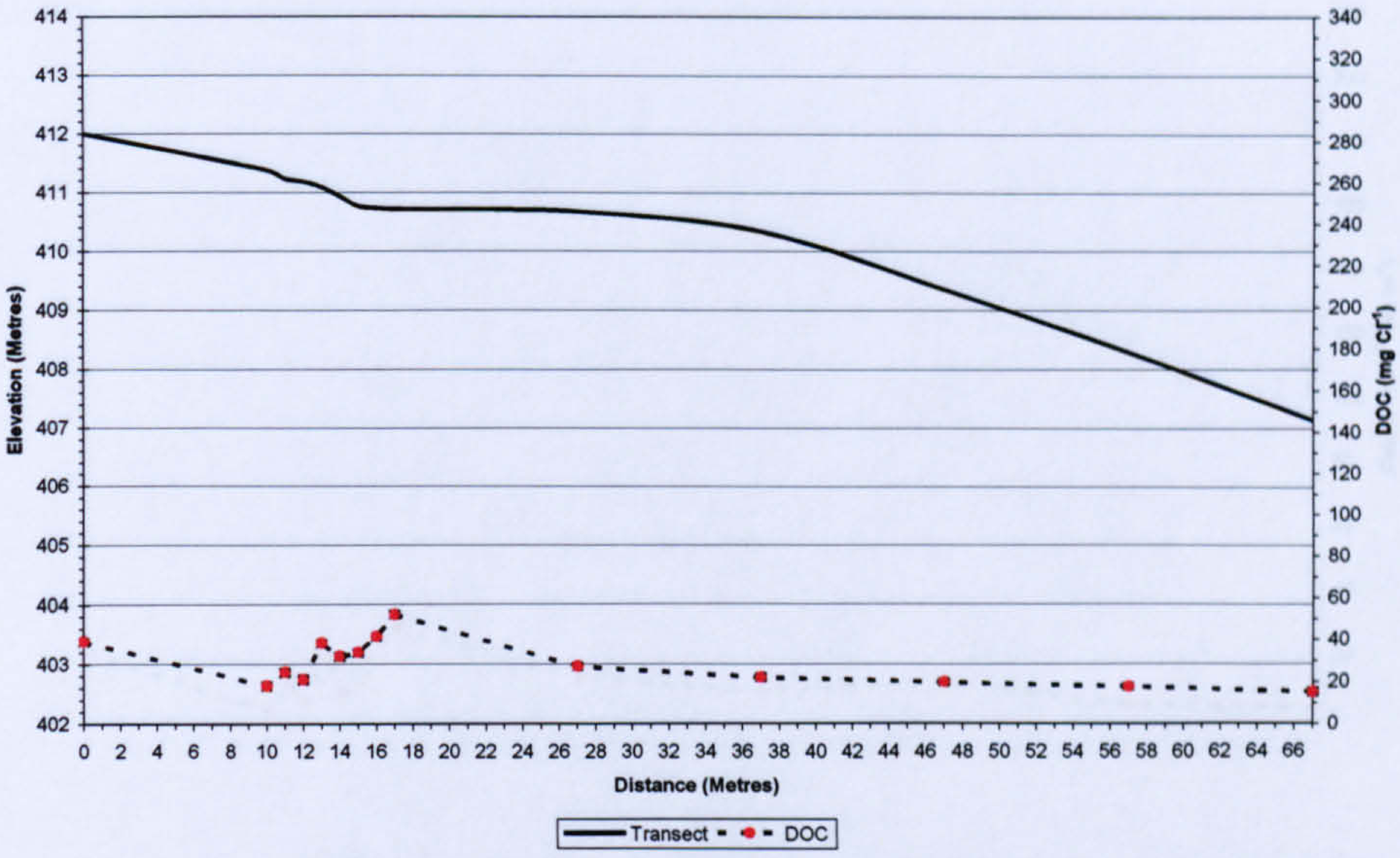


Figure 4.61 How DOC at 20 cm varies across the intact transect. Vertical bars represent the SE mean.

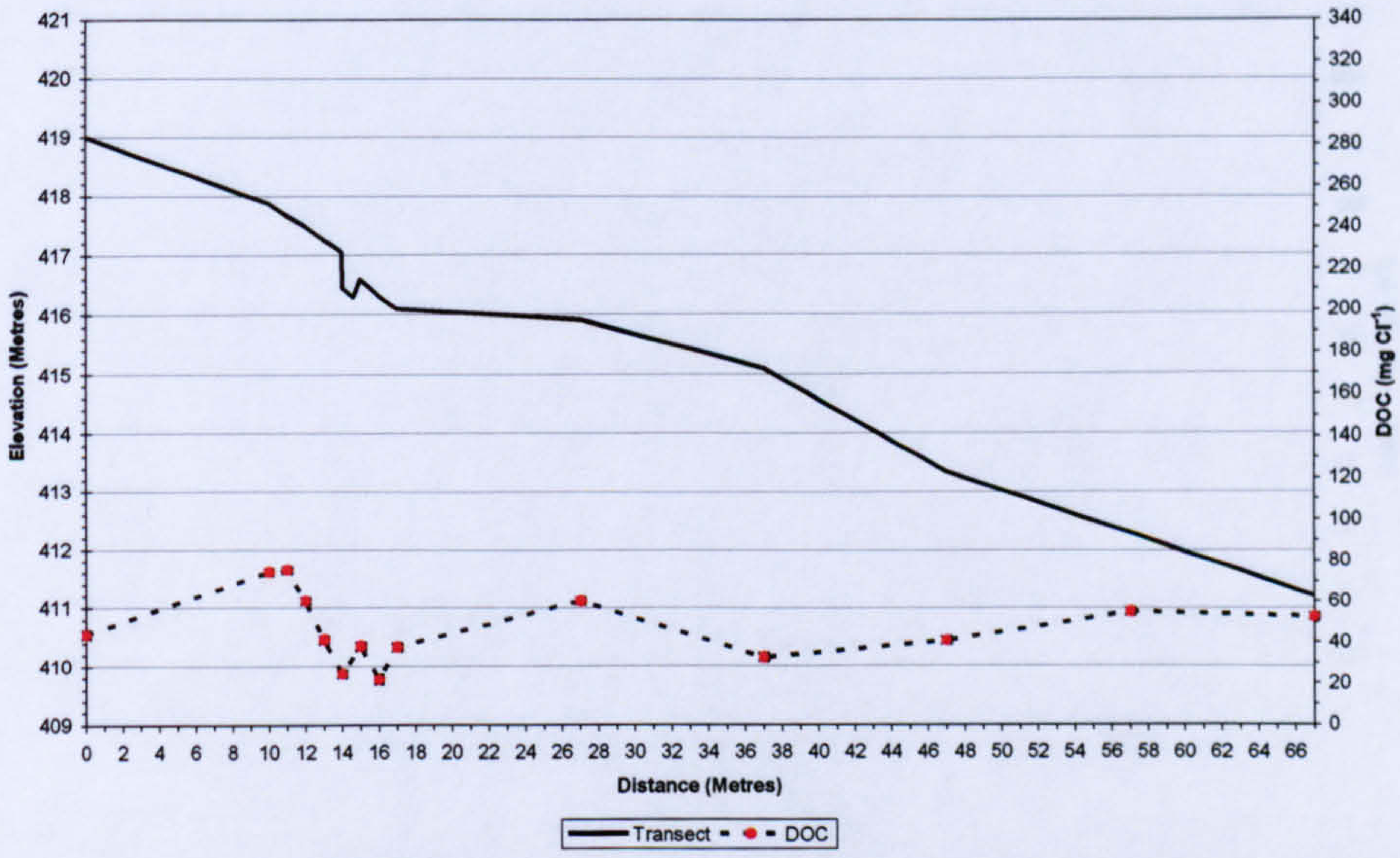


Figure 4.62 How DOC at 20cm varies across the drained transect. Vertical bars represent the SE mean.

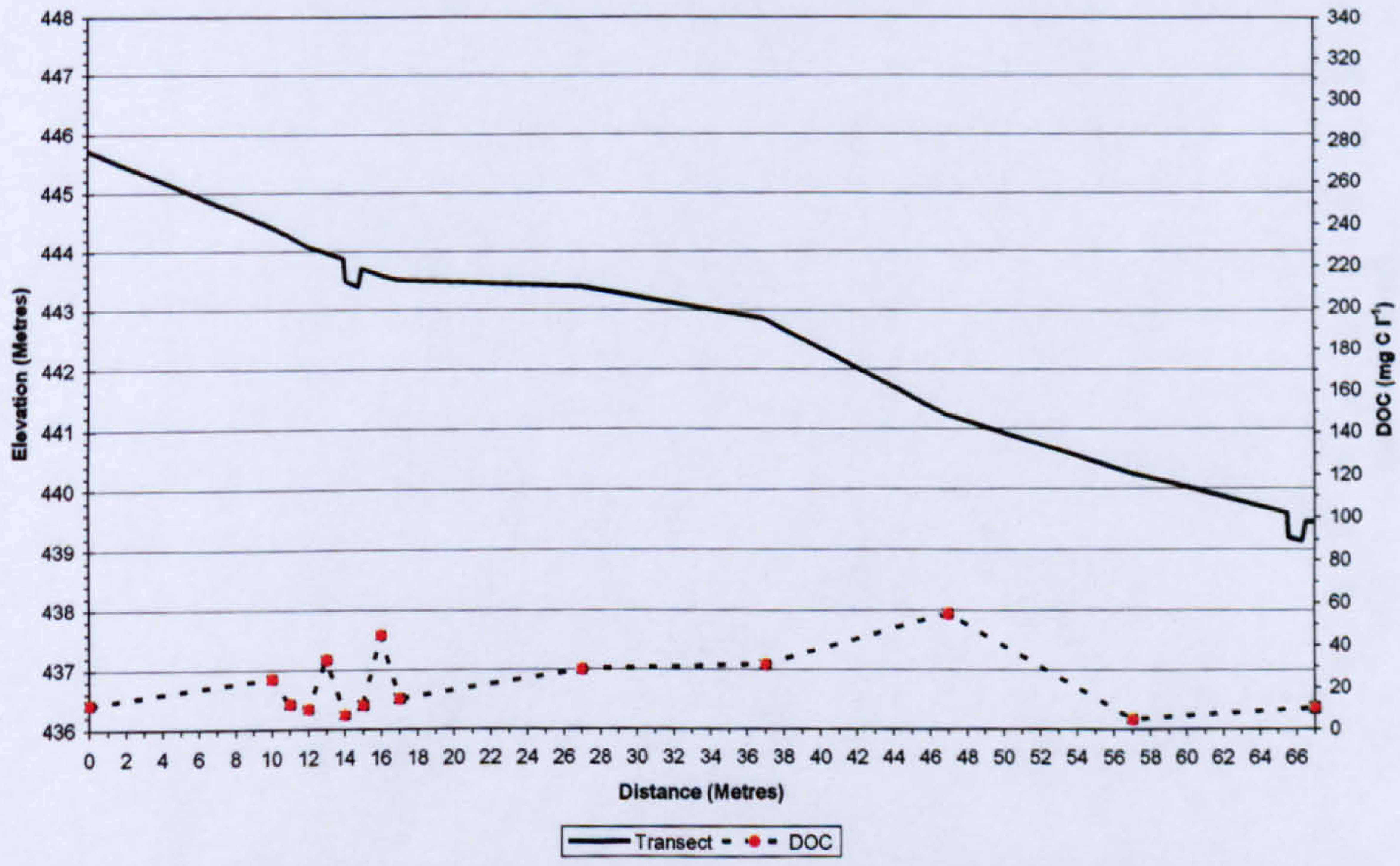


Figure 4.63 How DOC at 20cm varies across the blocked transect. Vertical bars represent the SE mean.

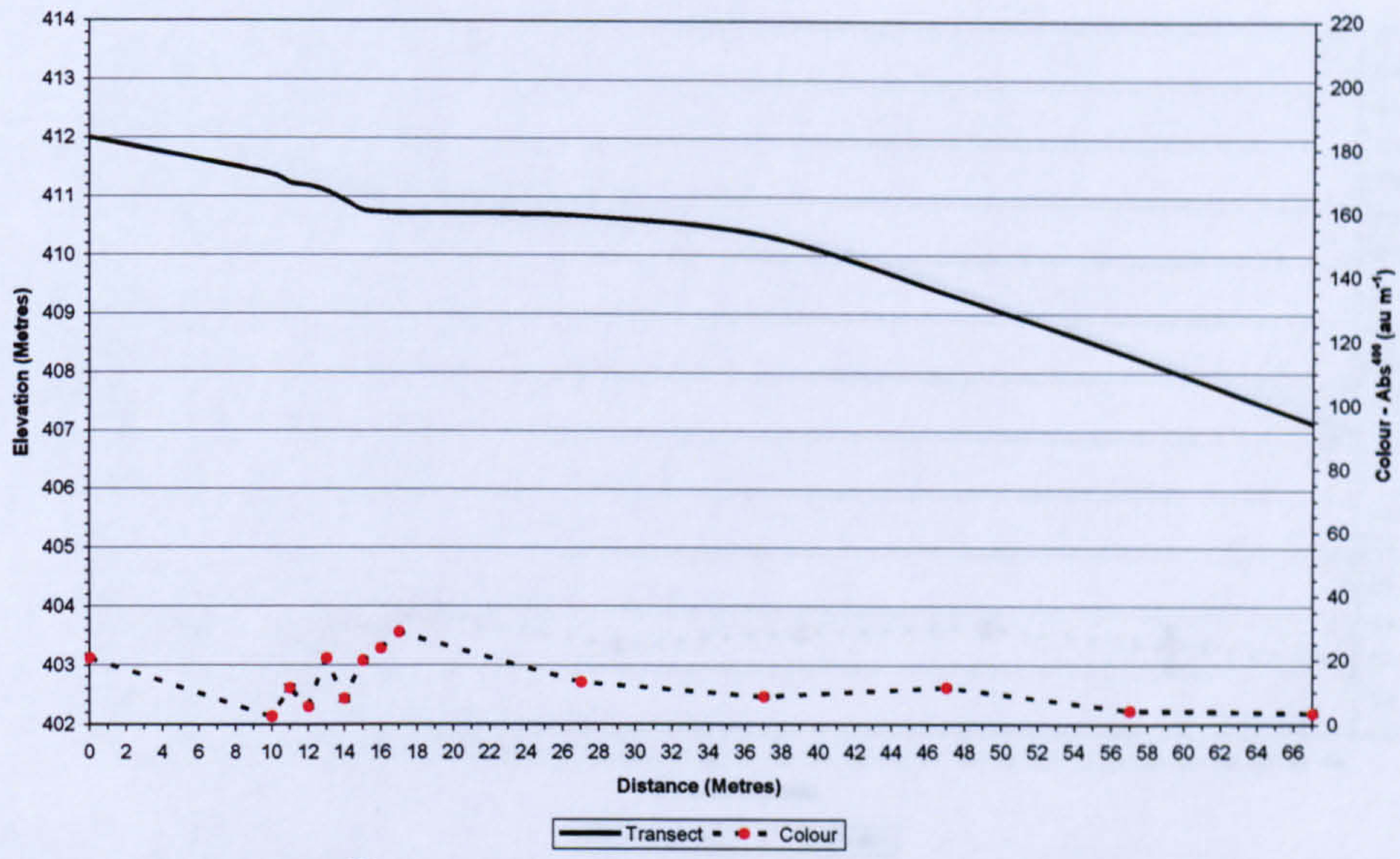


Figure 4.64 How colour (Abs^{400}) at 20cm varies across the intact transect. Vertical bars represent the SE mean.

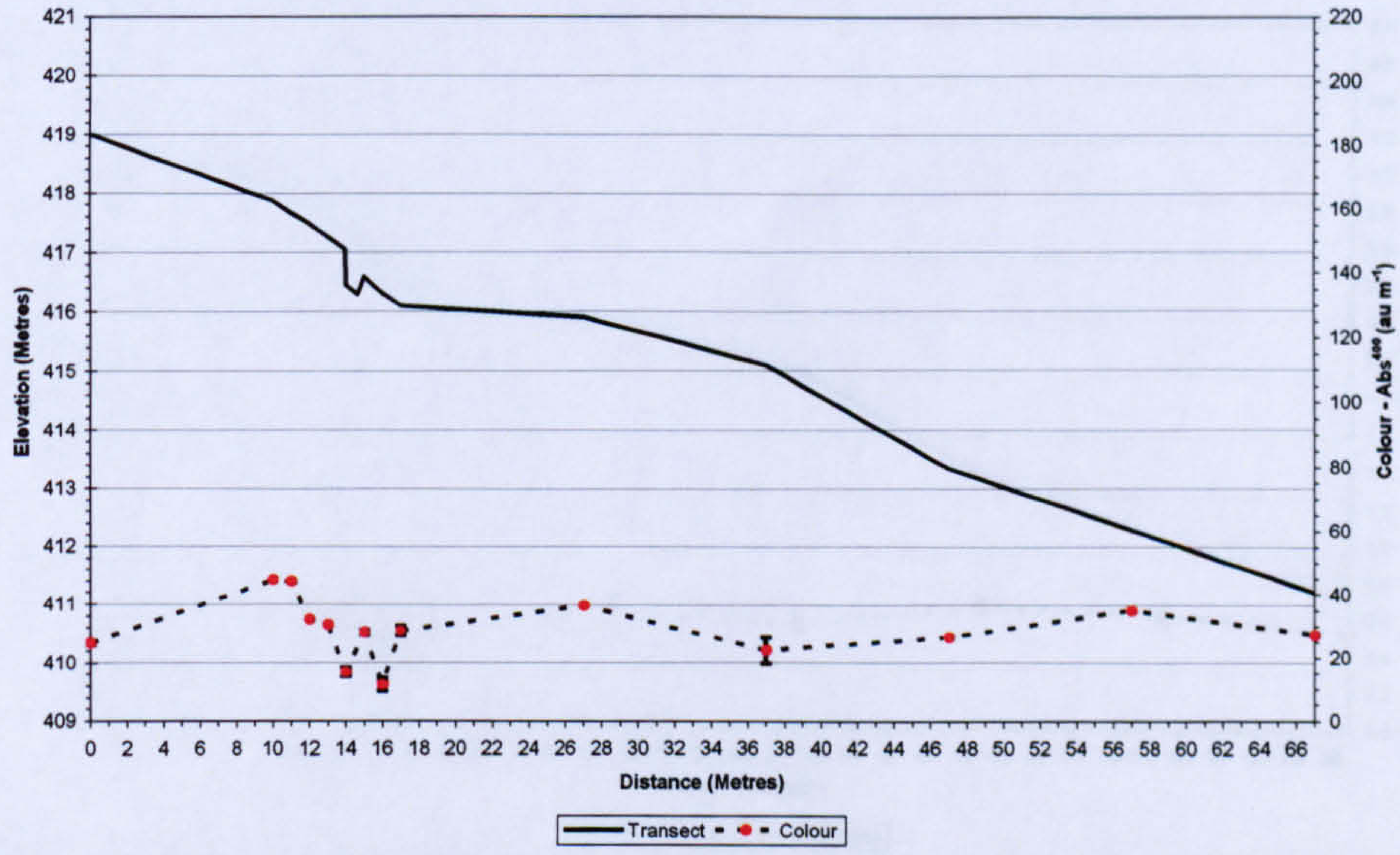


Figure 4.65 How colour (Abs^{400}) at 20cm varies across the drained transect. Vertical bars represent the SE mean.

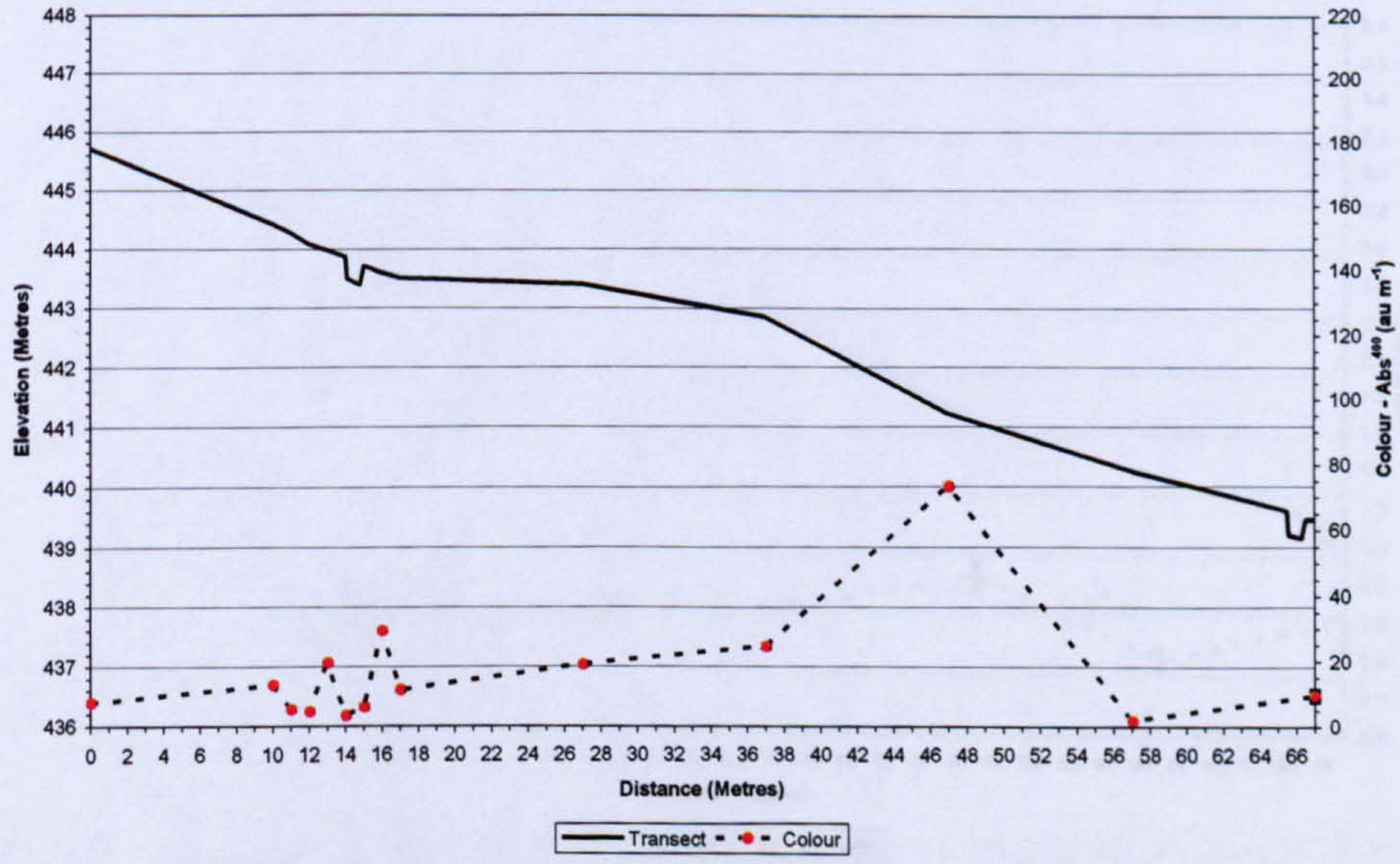


Figure 4.66 How colour (Abs^{400}) at 20cm varies across the blocked transect. Vertical bars represent the SE mean..

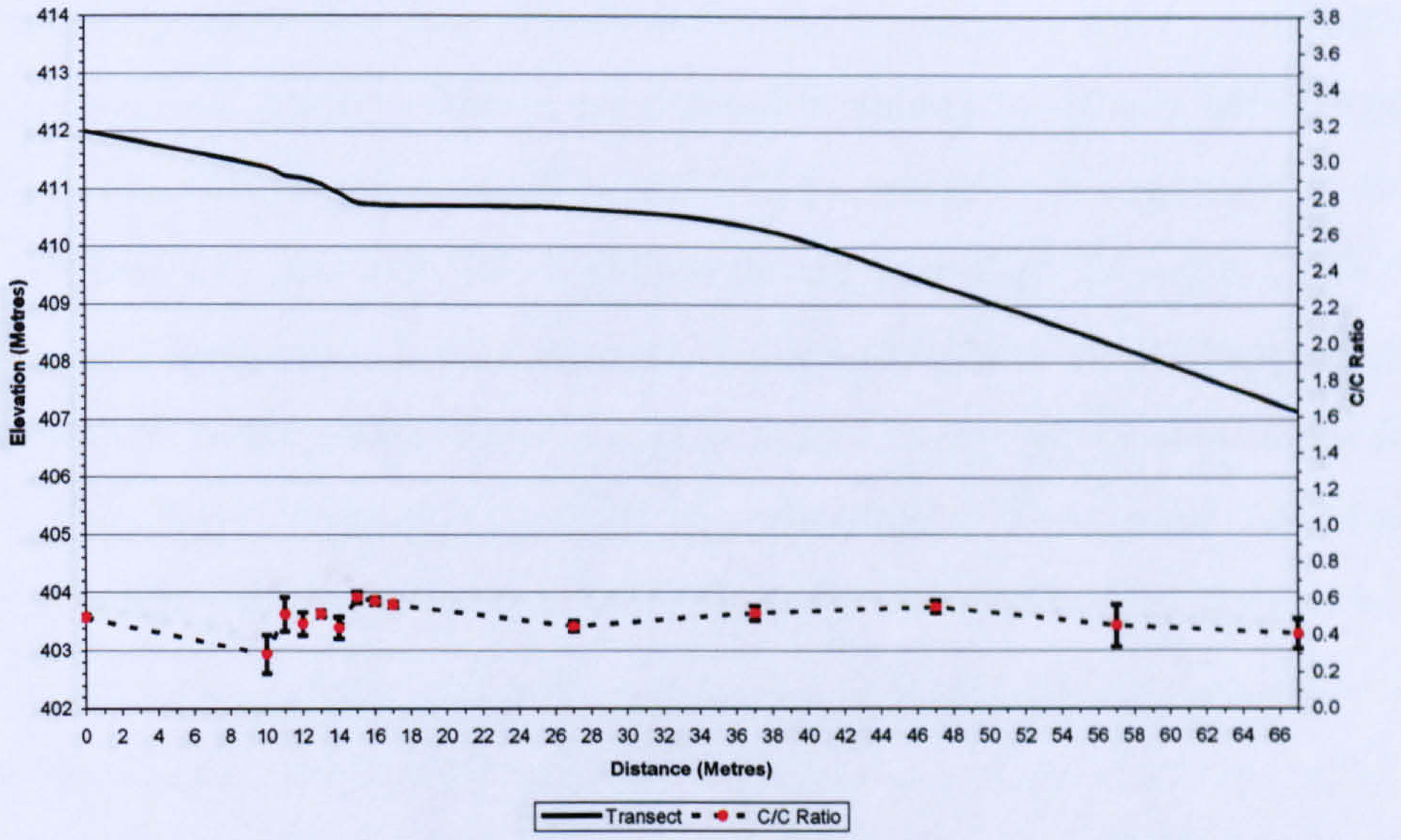


Figure 4.67 How the C/C ratio at 20cm varies across the intact transect. Vertical bars represent the SE mean.

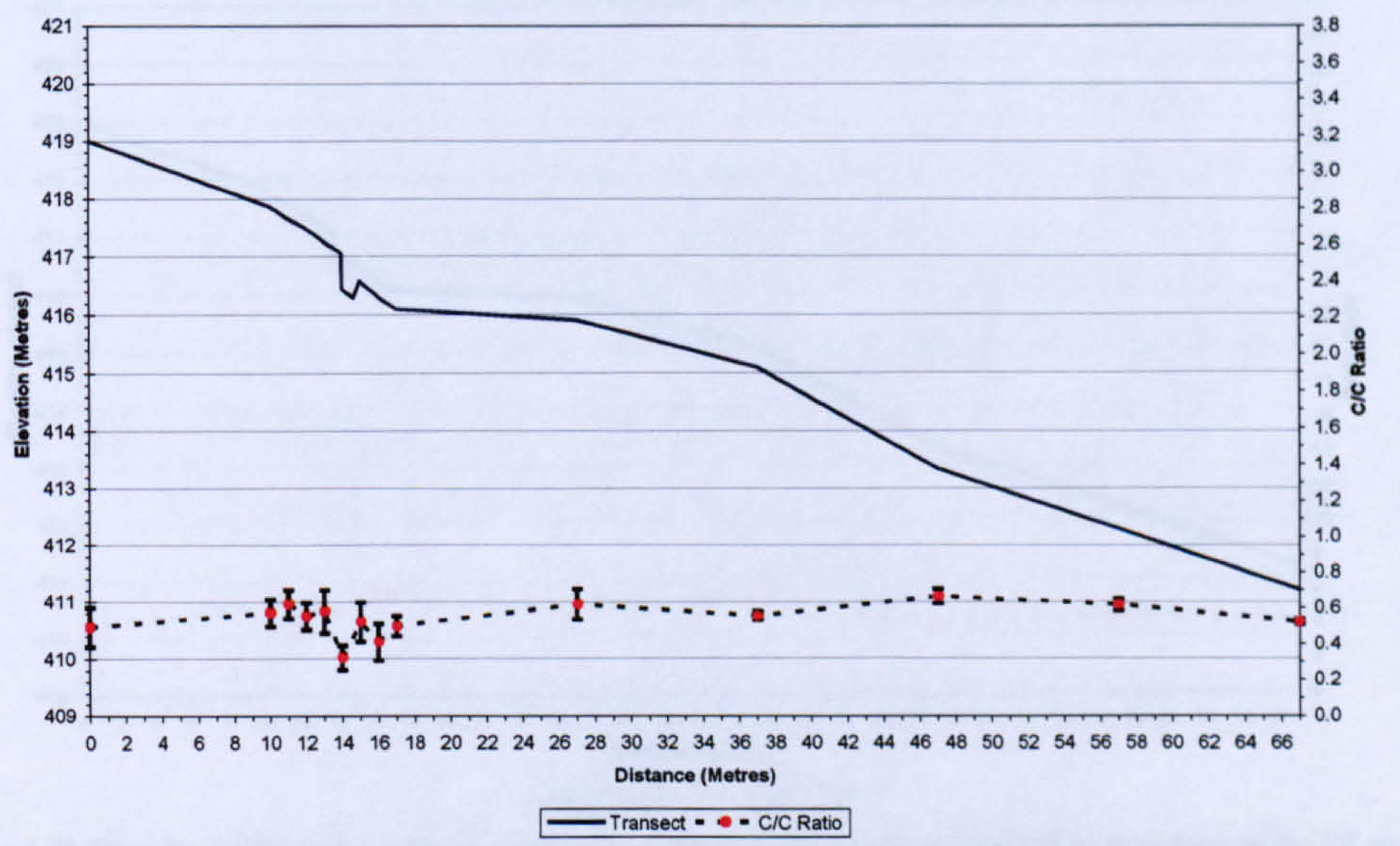


Figure 4.68 How the C/C ratio at 20cm varies across the drained transect. Vertical bars represent the SE mean.

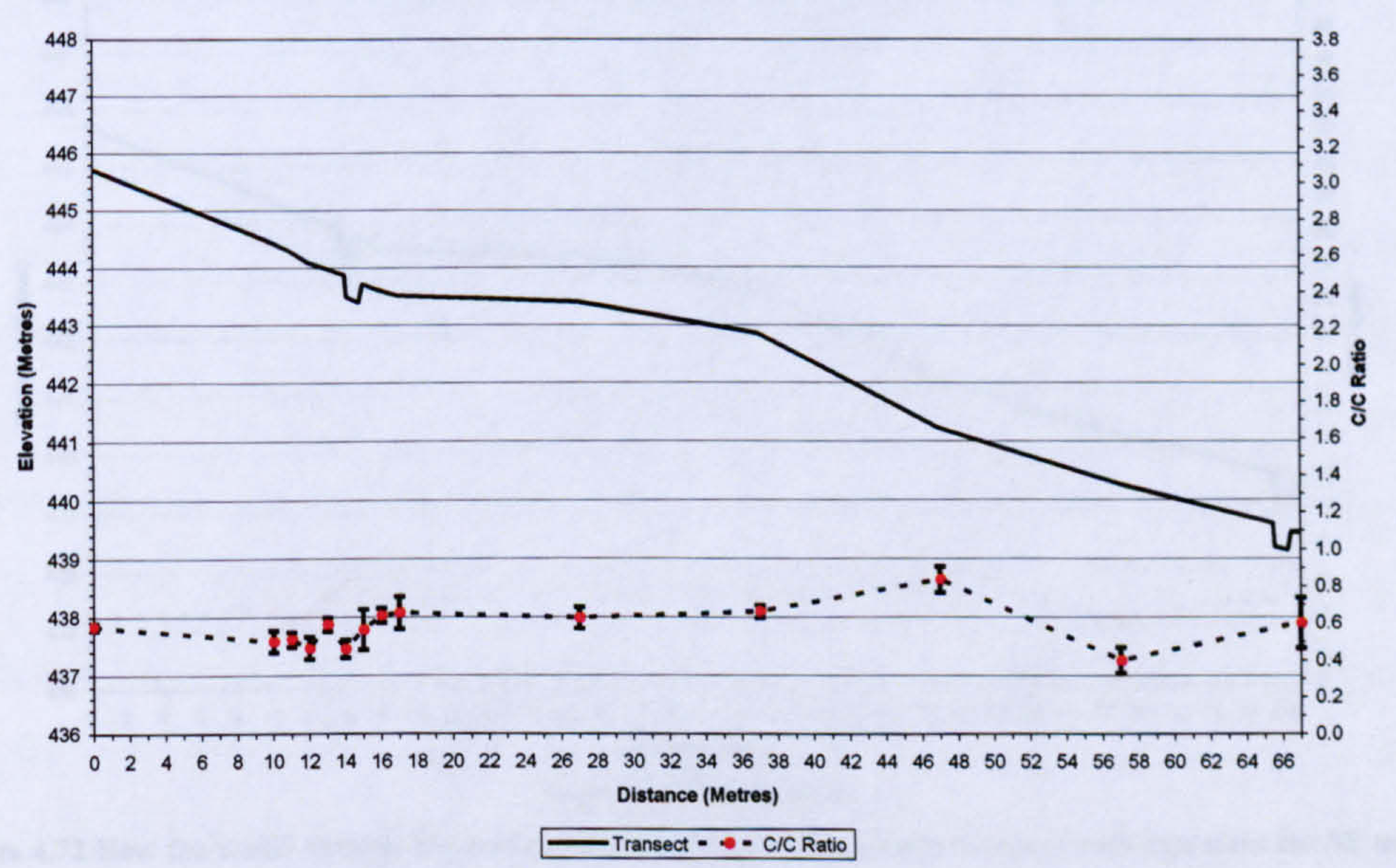


Figure 4.69 How the C/C ratio at 20cm varies across the blocked transect. Vertical bars represent the SE mean.

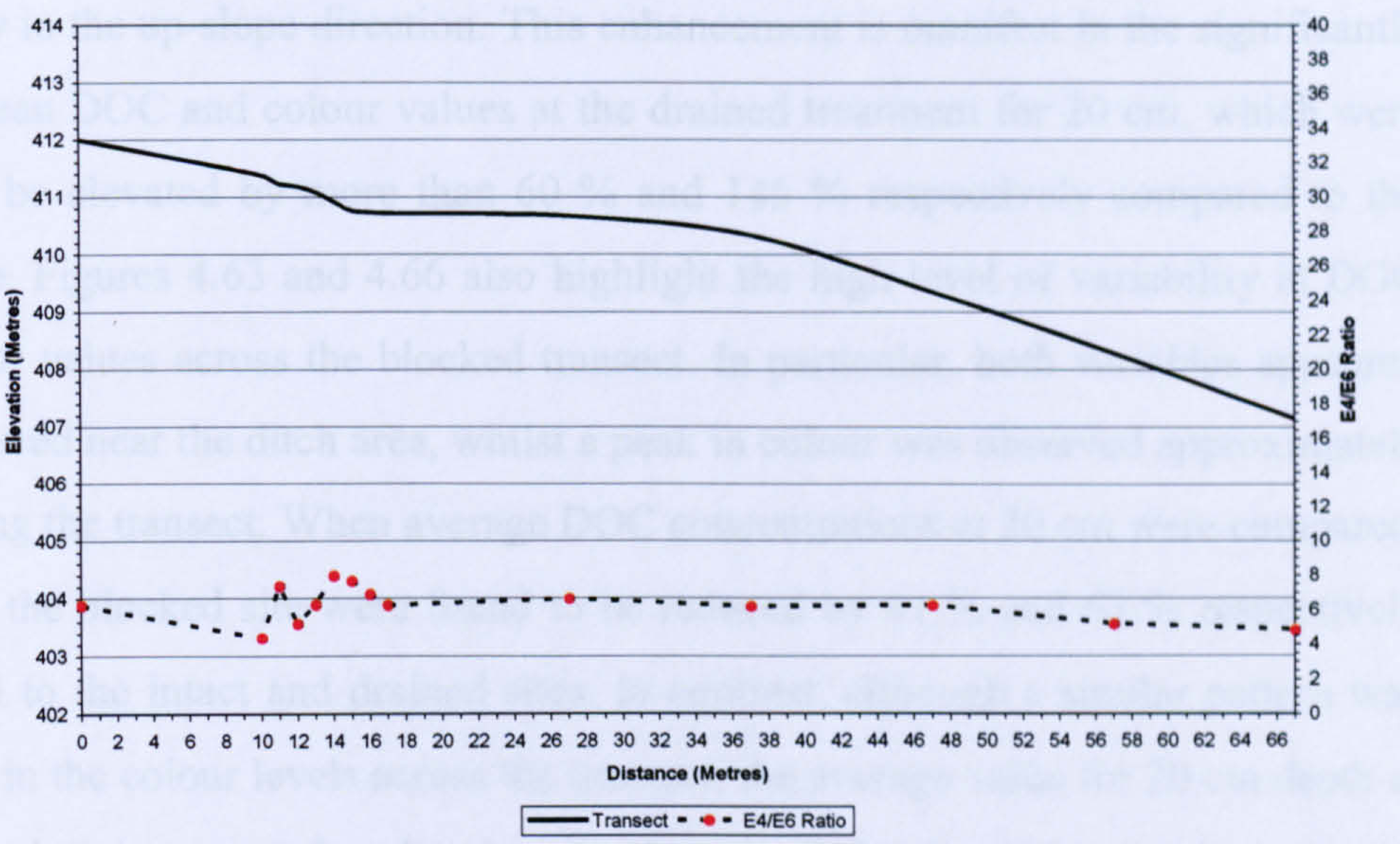


Figure 4.70 How the E4/E6 ratio at 20cm varies across the intact transect. Vertical bars represent the SE mean.

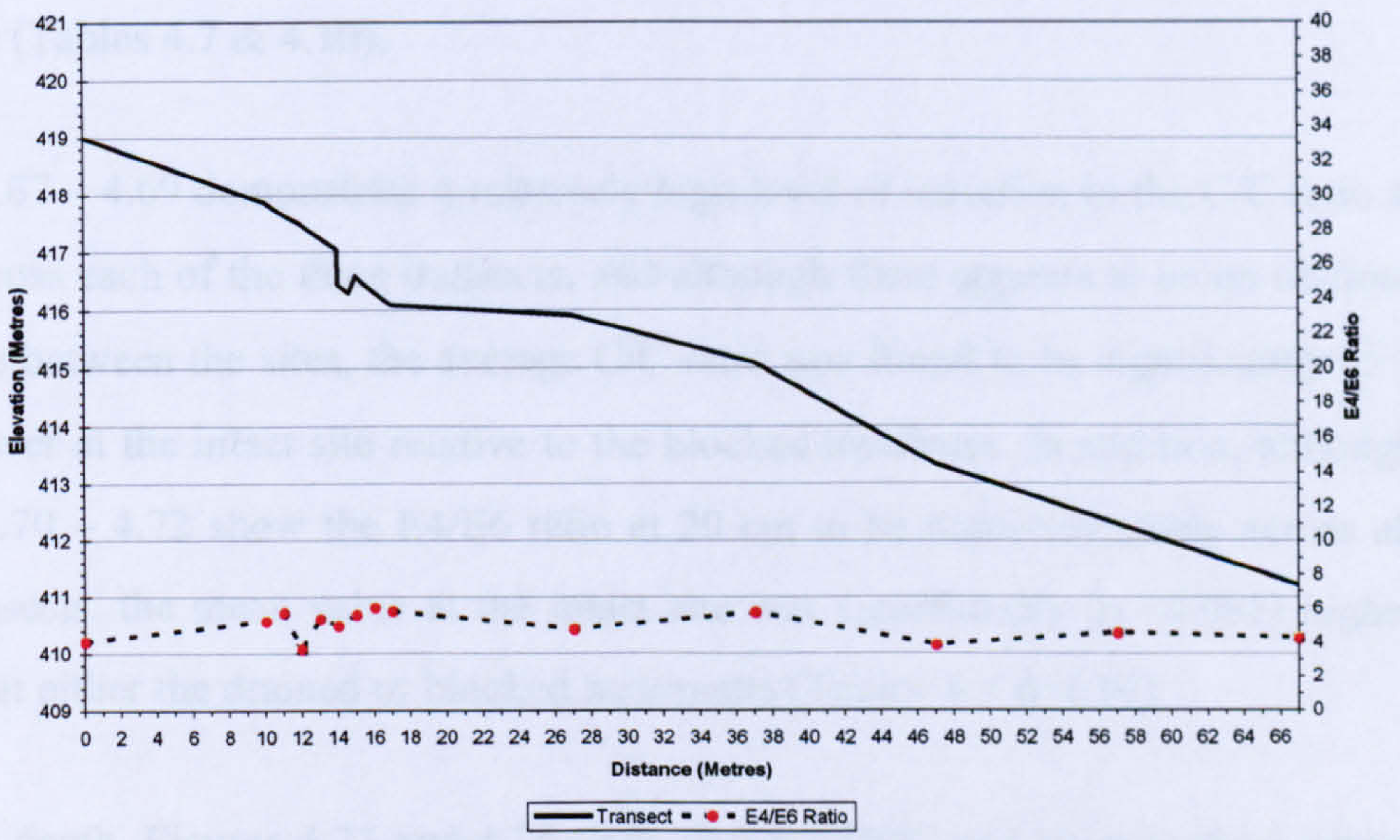


Figure 4.71 How the E4/E6 ratio at 20cm varies across the drained transect. Vertical bars represent the SE mean.

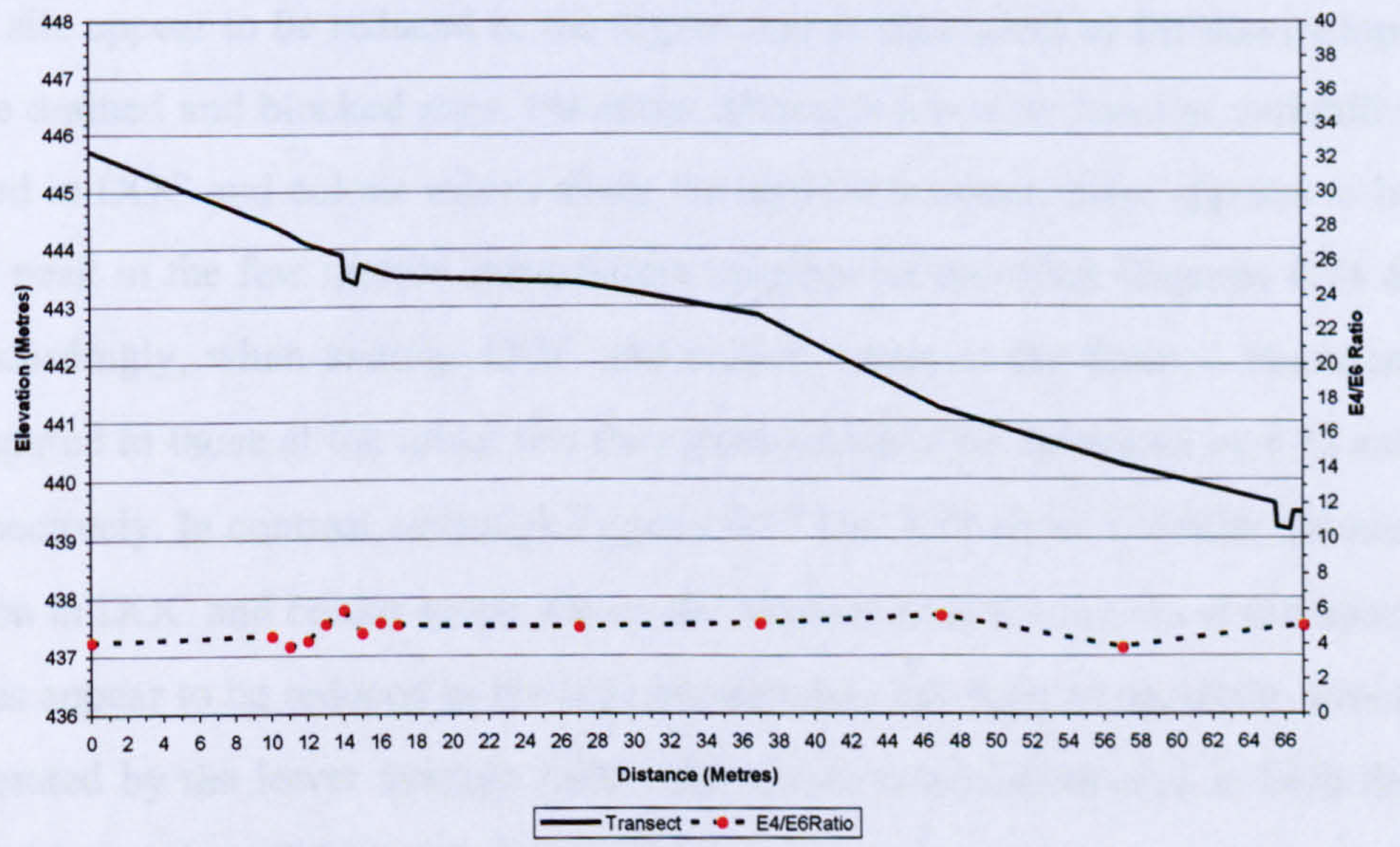


Figure 4.72 How the E4/E6 ratio at 20cm varies across the blocked transect. Vertical bars represent the SE mean.

especially in the up-slope direction. This enhancement is manifest in the significantly higher mean DOC and colour values at the drained treatment for 20 cm, which were found to be elevated by more than 60 % and 146 % respectively compared to the intact site. Figures 4.63 and 4.66 also highlight the high level of variability in DOC and colour values across the blocked transect. In particular, both variables appeared to be reduced near the ditch area, whilst a peak in colour was observed approximately 48 m along the transect. When average DOC concentrations at 20 cm were compared, values at the blocked site were found to be reduced by 41 % and 63 % respectively compared to the intact and drained sites. In contrast, although a similar pattern was observed in the colour levels across the transect, the average value for 20 cm depth at the blocked site was not found to be significantly different to that observed for the intact site (Tables 4.7 & 4.10).

Figures 4.67 – 4.69 demonstrate a relatively high level of variation in the C/C ratio at 20 cm across each of the three transects, and although there appears to be no obvious difference between the sites, the average C/C ratio was found to be significantly (p = 0.007) lower at the intact site relative to the blocked treatment. In addition, although Figures 4.70 – 4.72 show the E4/E6 ratio at 20 cm to be relatively stable across all three transects, the mean value at the intact site was significantly (p <0.001) higher than that at either the drained or blocked treatments (Tables 4.9 & 4.10).

At 40 cm depth, Figures 4.73 and 4.76 show that the DOC and colour values across the intact site appear to be reduced in the region that is equivalent to the down-slope area at the drained and blocked sites. However, although a similar level of variability is observed in DOC and colour values along the drained transect, there appears to be a definite peak in the few metres immediately up-slope of the ditch (Figures 4.74 & 4.77). Accordingly, when average DOC and colour values at the drained treatment were compared to those at the intact site they were found to be enhanced by 6 % and 32 % respectively. In contrast, although Figures 4.75 and 4.78 show a similar amount of variation in DOC and colour levels across the blocked transect as seen at the intact site, values appear to be reduced in the area immediately up-slope of the ditch, which is corroborated by the lower average DOC and colour values compared to both the drained and intact sites (Tables 4.6, 4.7 & 4.10).

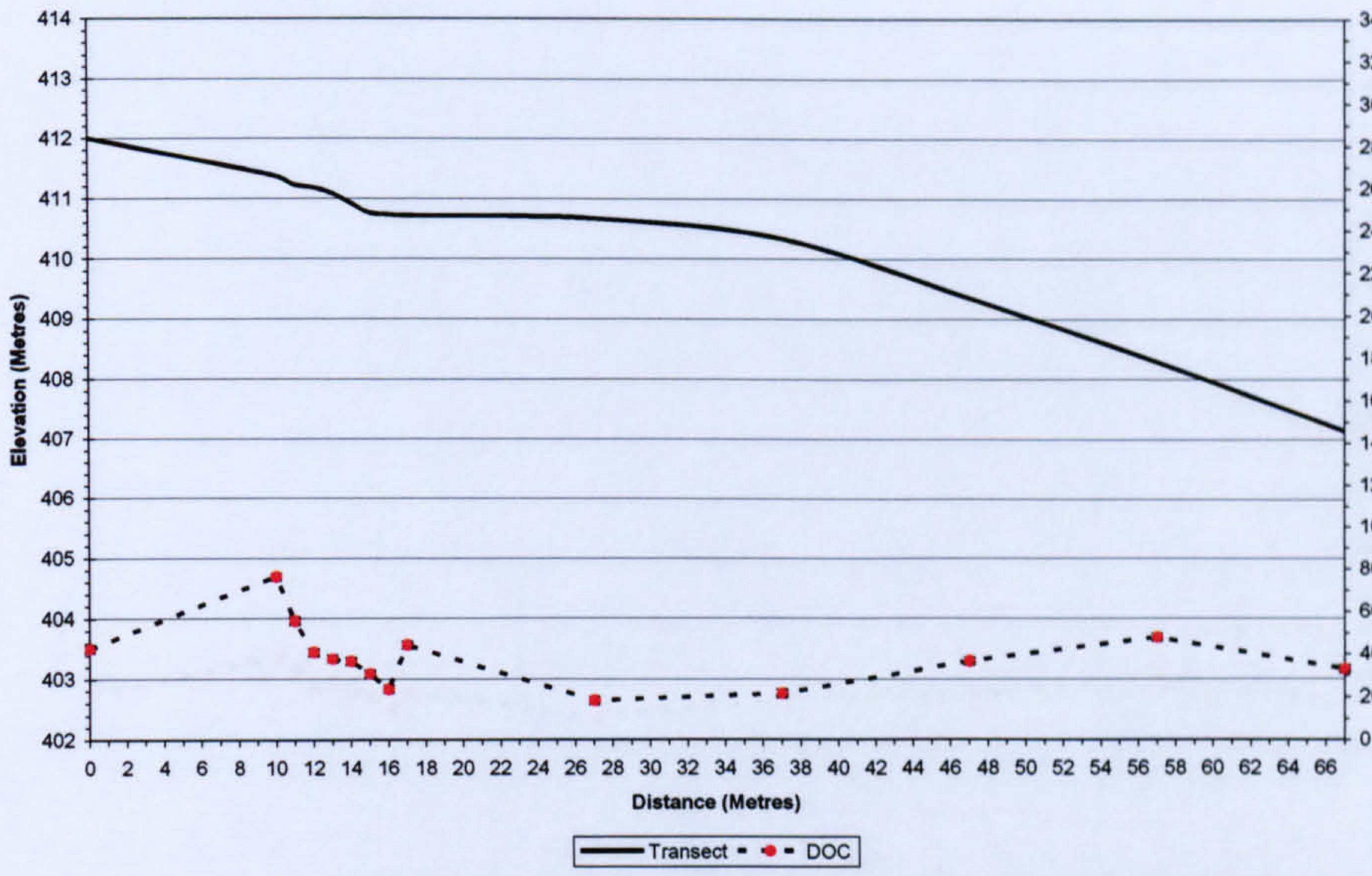


Figure 4.73 How DOC at 40 cm varies across the intact transect. Vertical bars represent the SE mean.

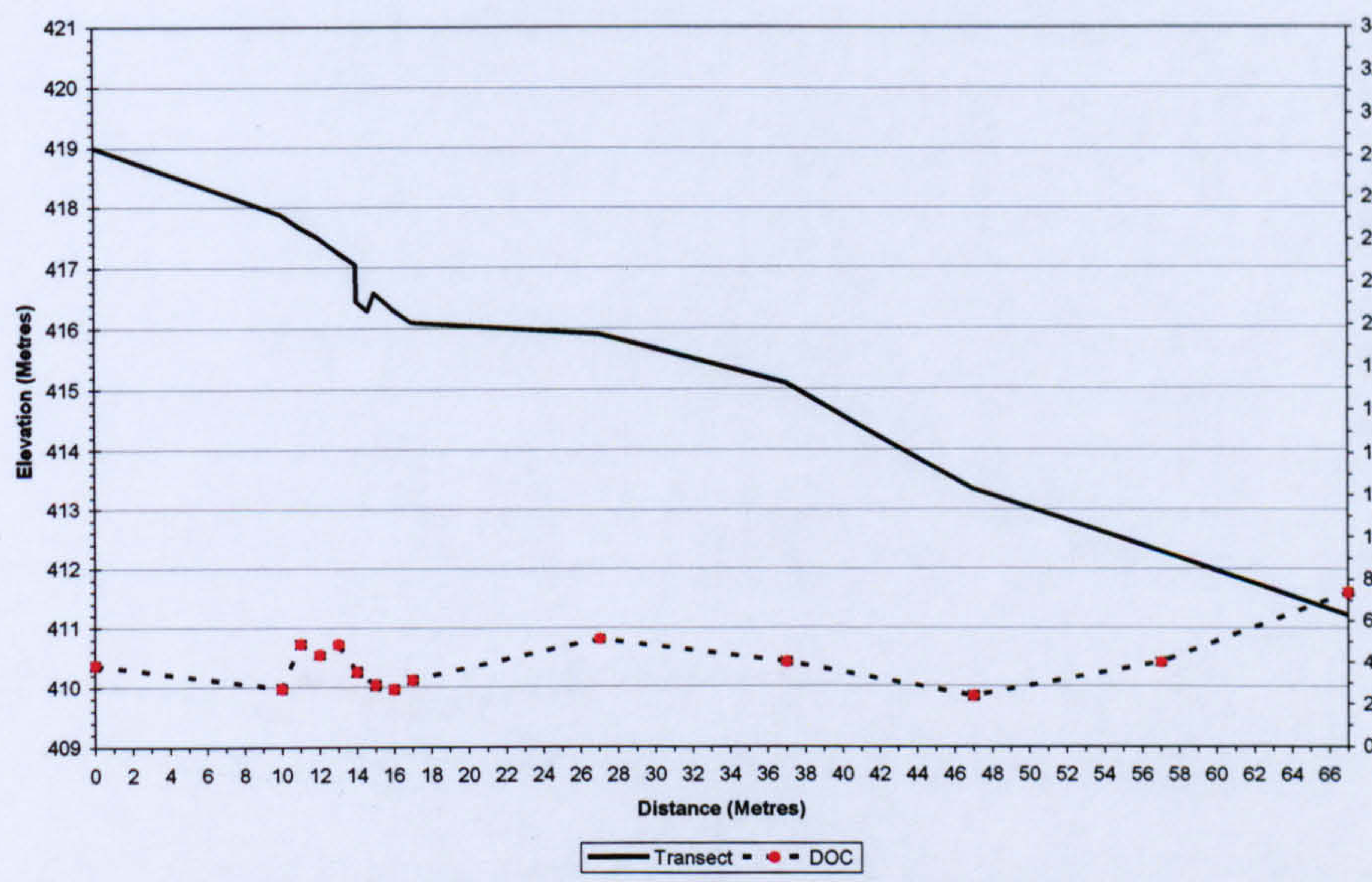


Figure 4.74 How DOC at 40cm varies across the drained transect. Vertical bars represent the SE mean.

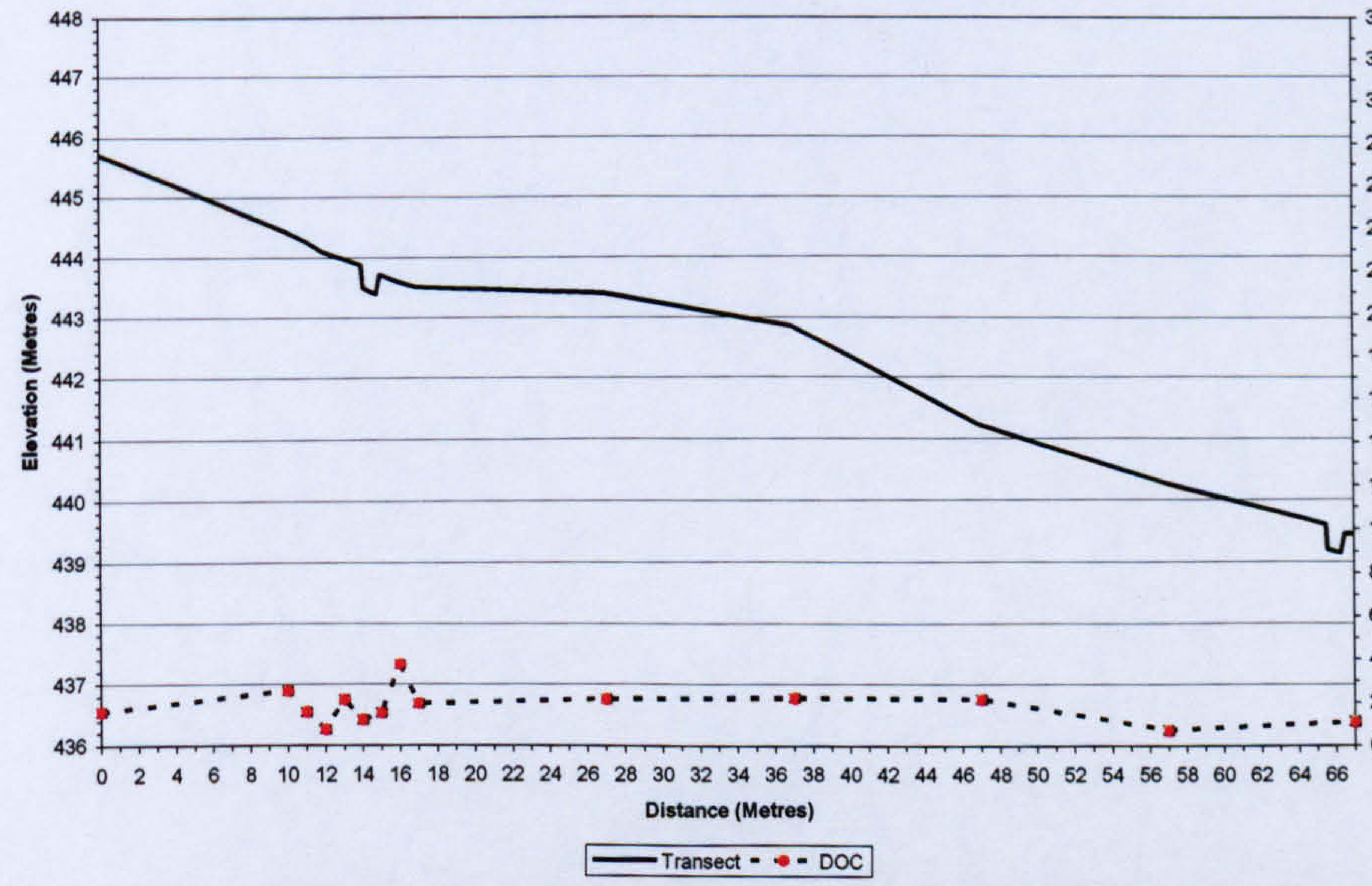


Figure 4.75 How DOC at 40cm varies across the blocked transect. Vertical bars represent the SE mean.

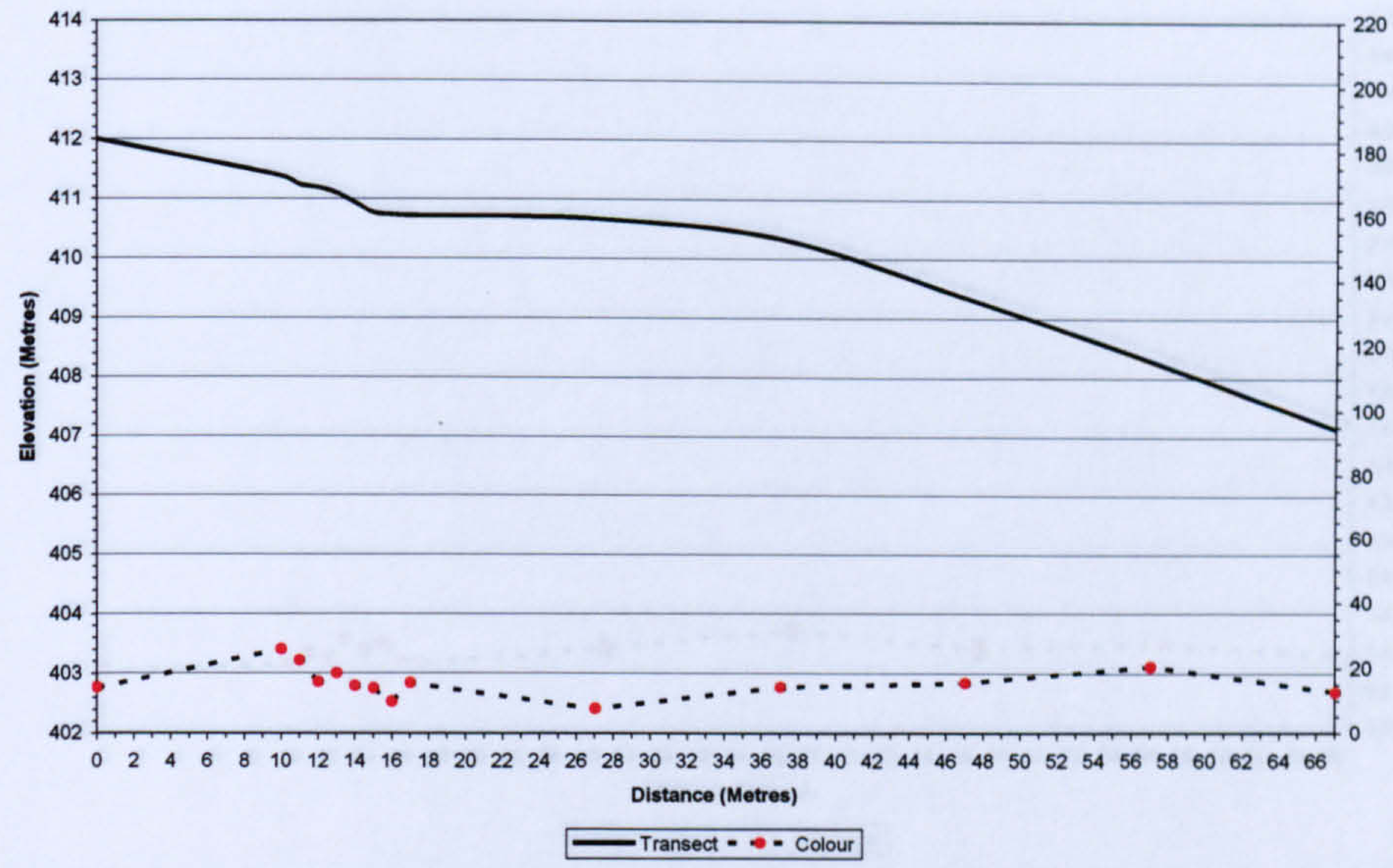


Figure 4.76 How colour (Abs^{400}) at 40cm varies across the intact transect. Vertical bars represent the SE mean.

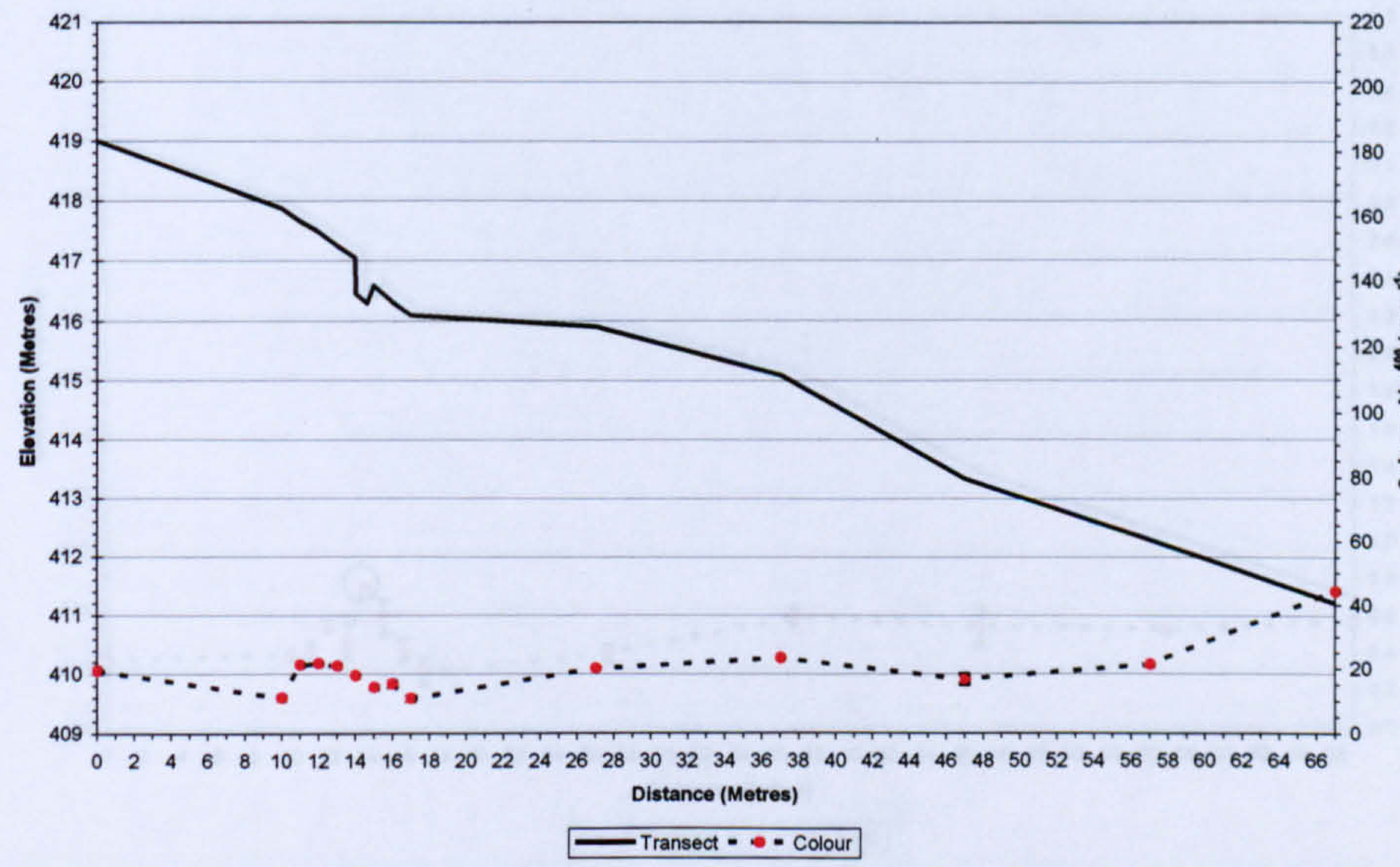


Figure 4.77 How colour (Abs^{400}) at 40cm varies across the drained transect. Vertical bars represent the SE mean.

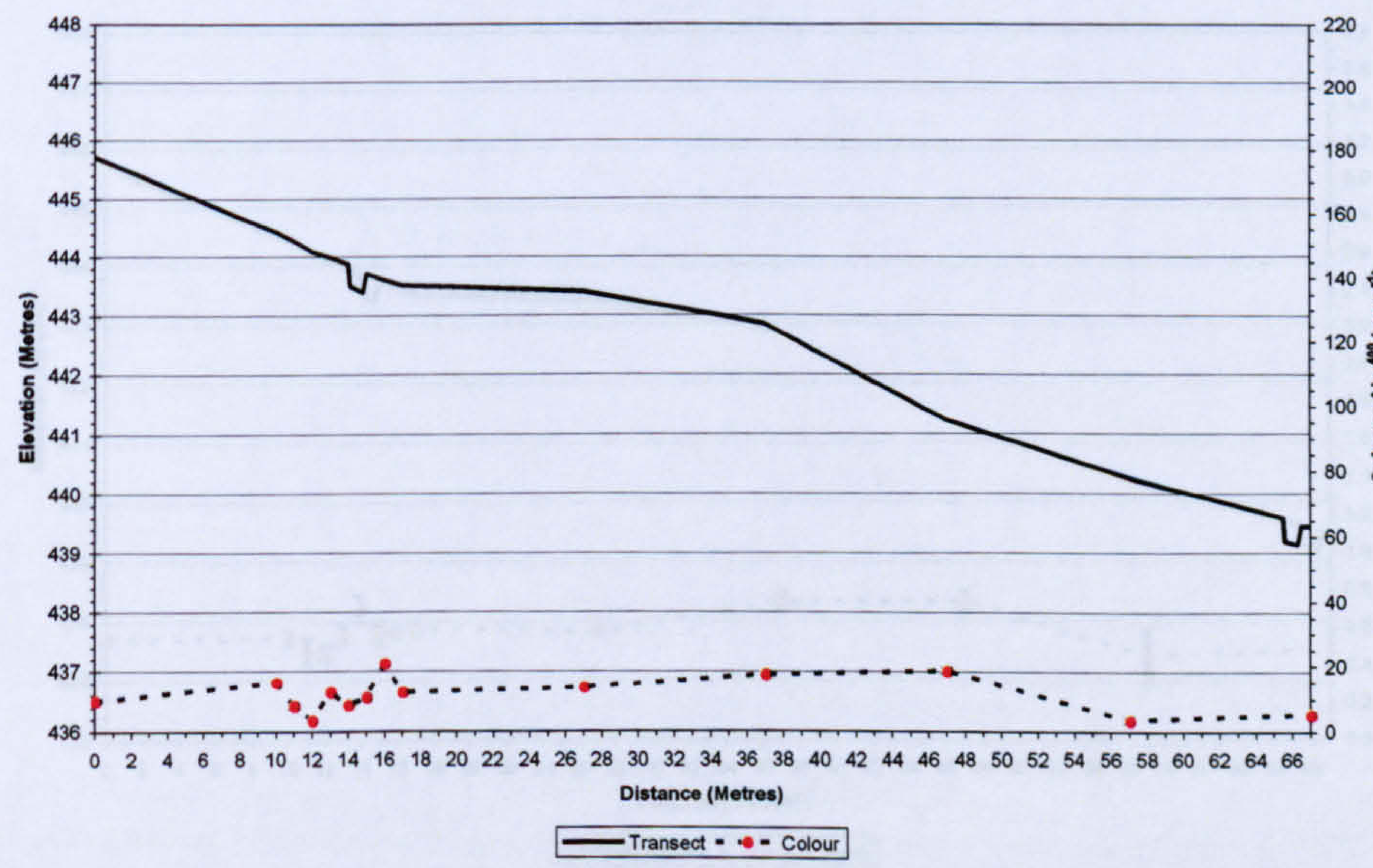


Figure 4.78 How colour (Abs^{400}) at 40cm varies across the blocked transect. Vertical bars represent the SE mean.

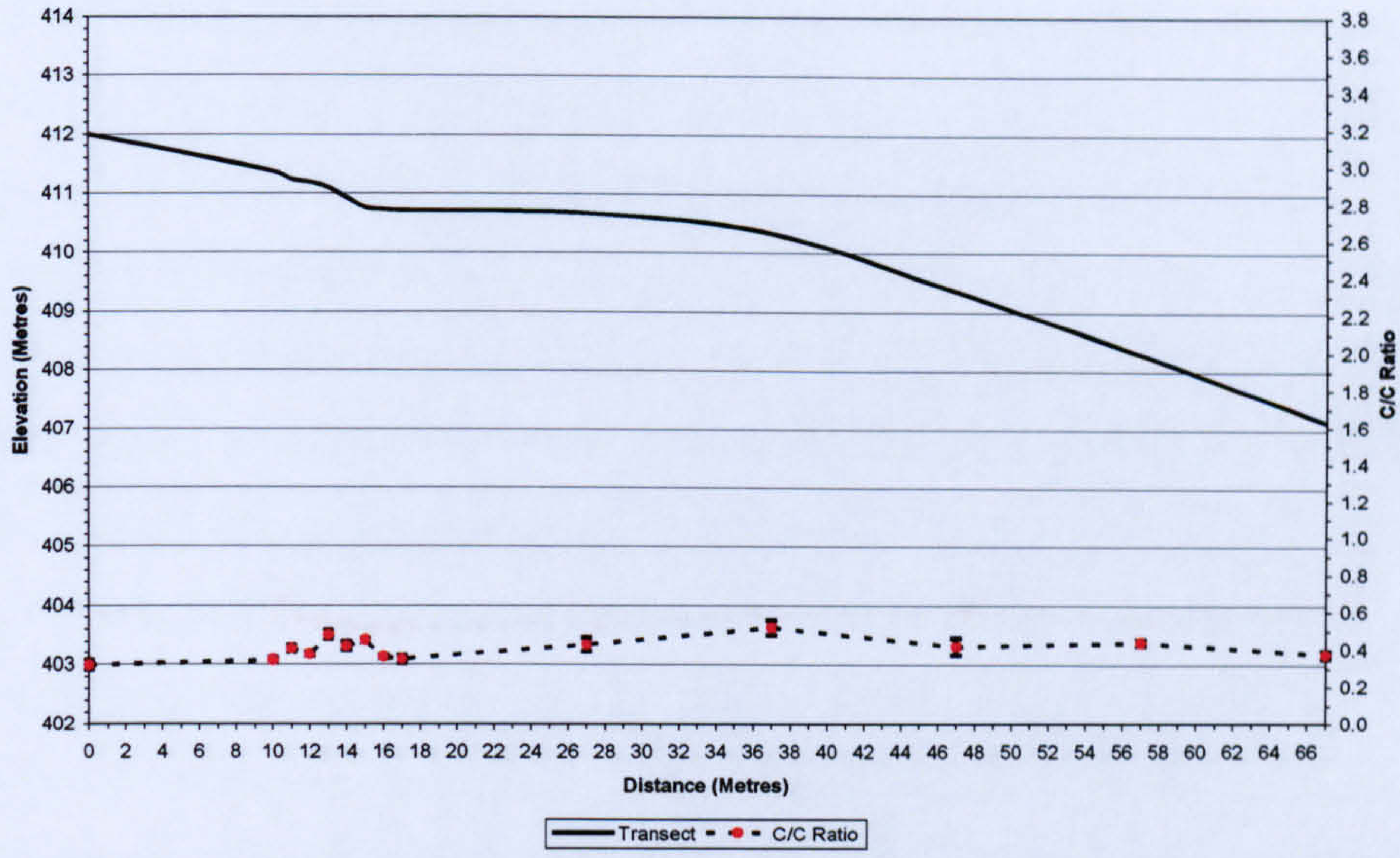


Figure 4.79 How the C/C ratio at 40cm varies across the intact transect. Vertical bars represent the SE mean.

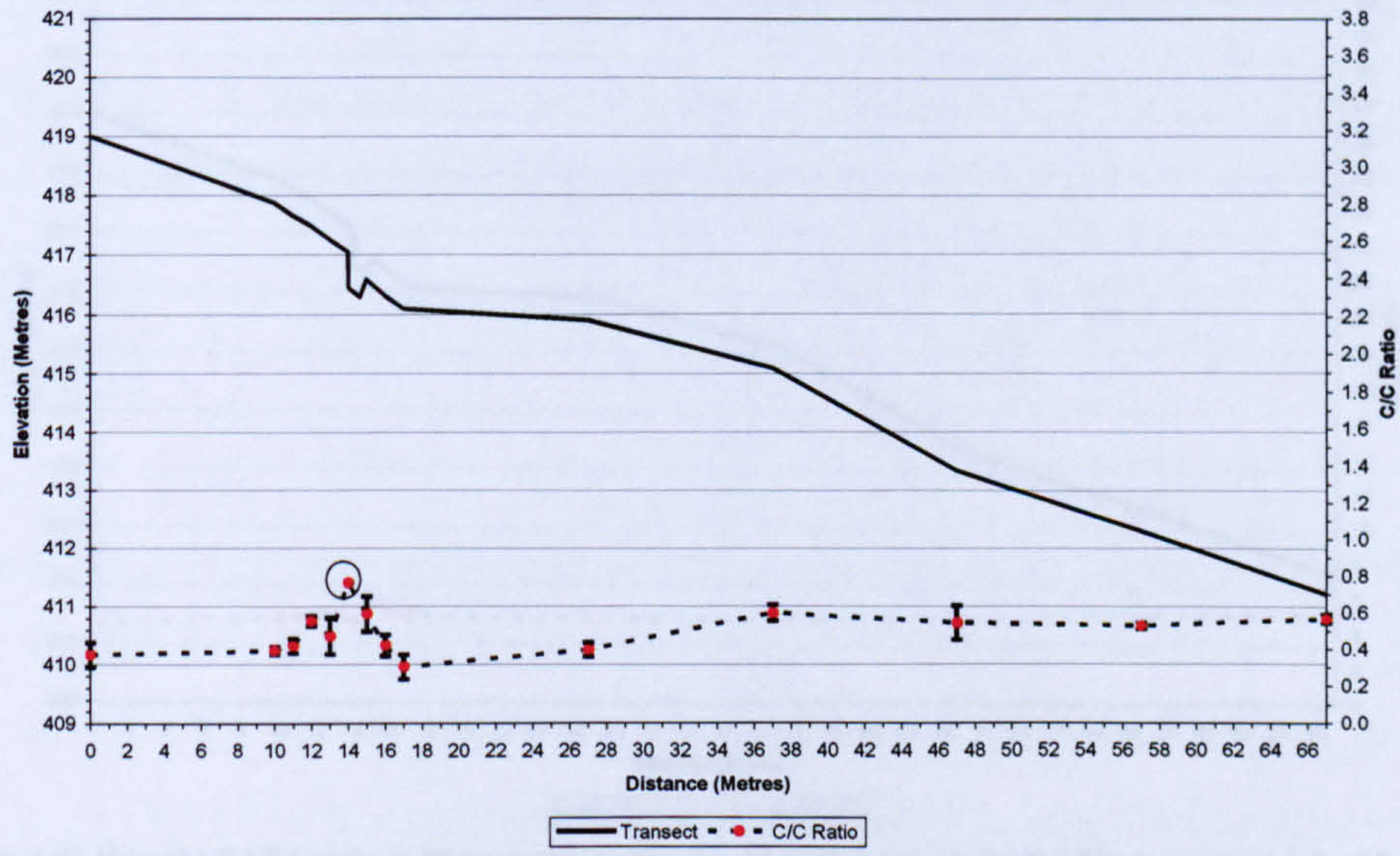


Figure 4.80 How the C/C ratio at 40cm varies across the drained transect. Vertical bars represent the SE mean, whilst circled values consist of data from only one sample.

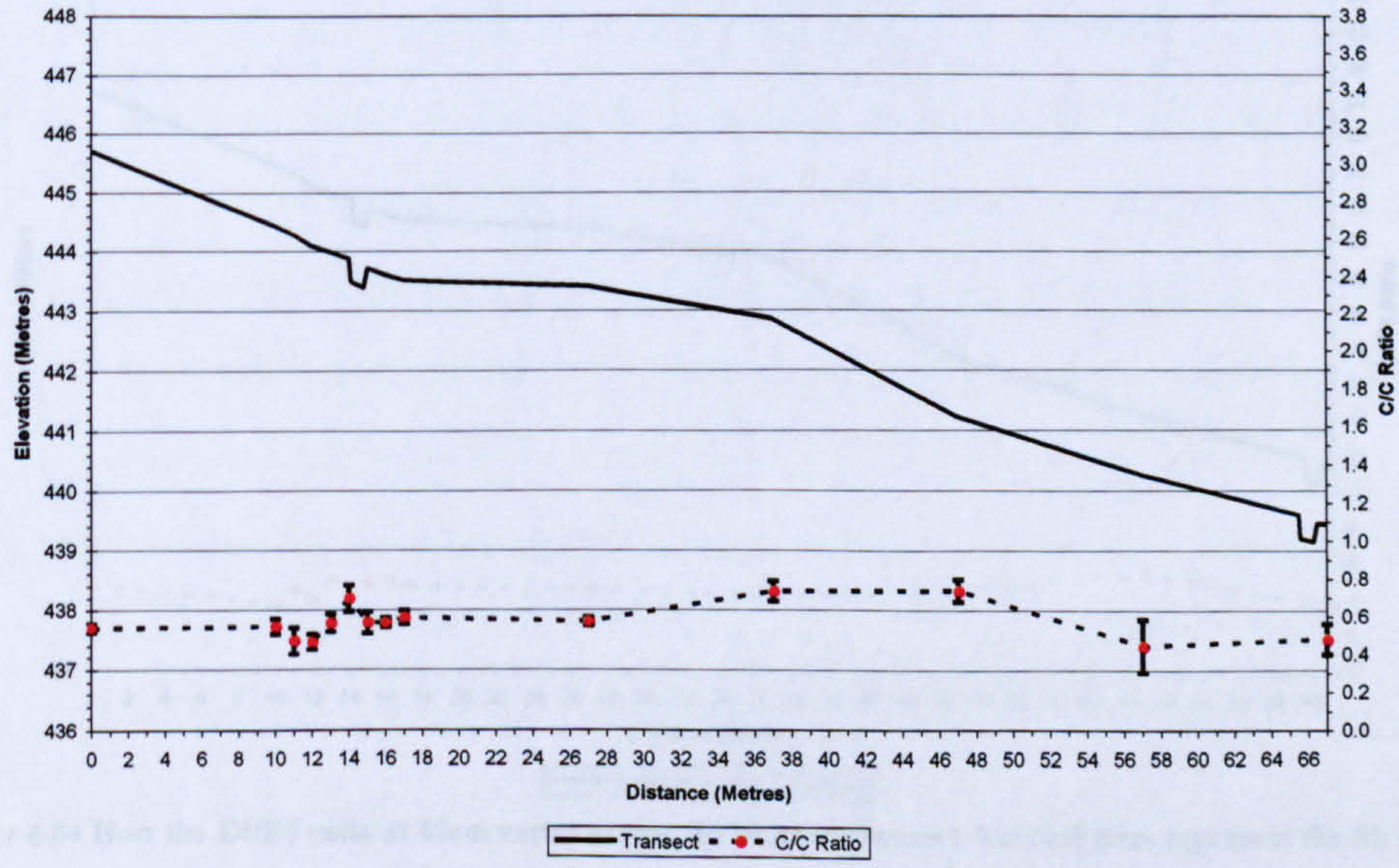


Figure 4.81 How the C/C ratio at 40cm varies across the blocked transect. Vertical bars represent the SE mean.

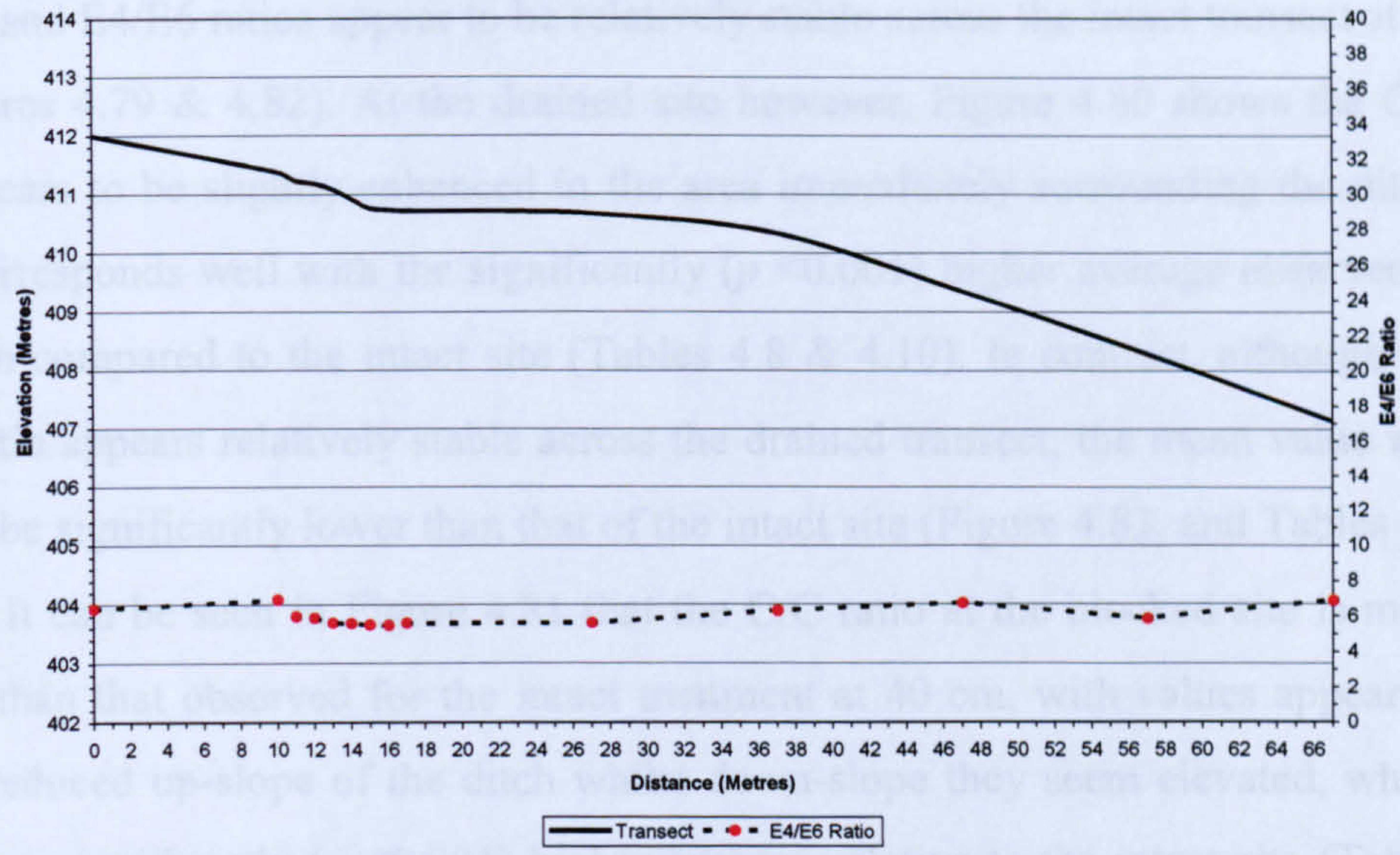


Figure 4.82 How the E4/E6 ratio at 40cm varies across the intact transect. Vertical bars represent the SE mean.

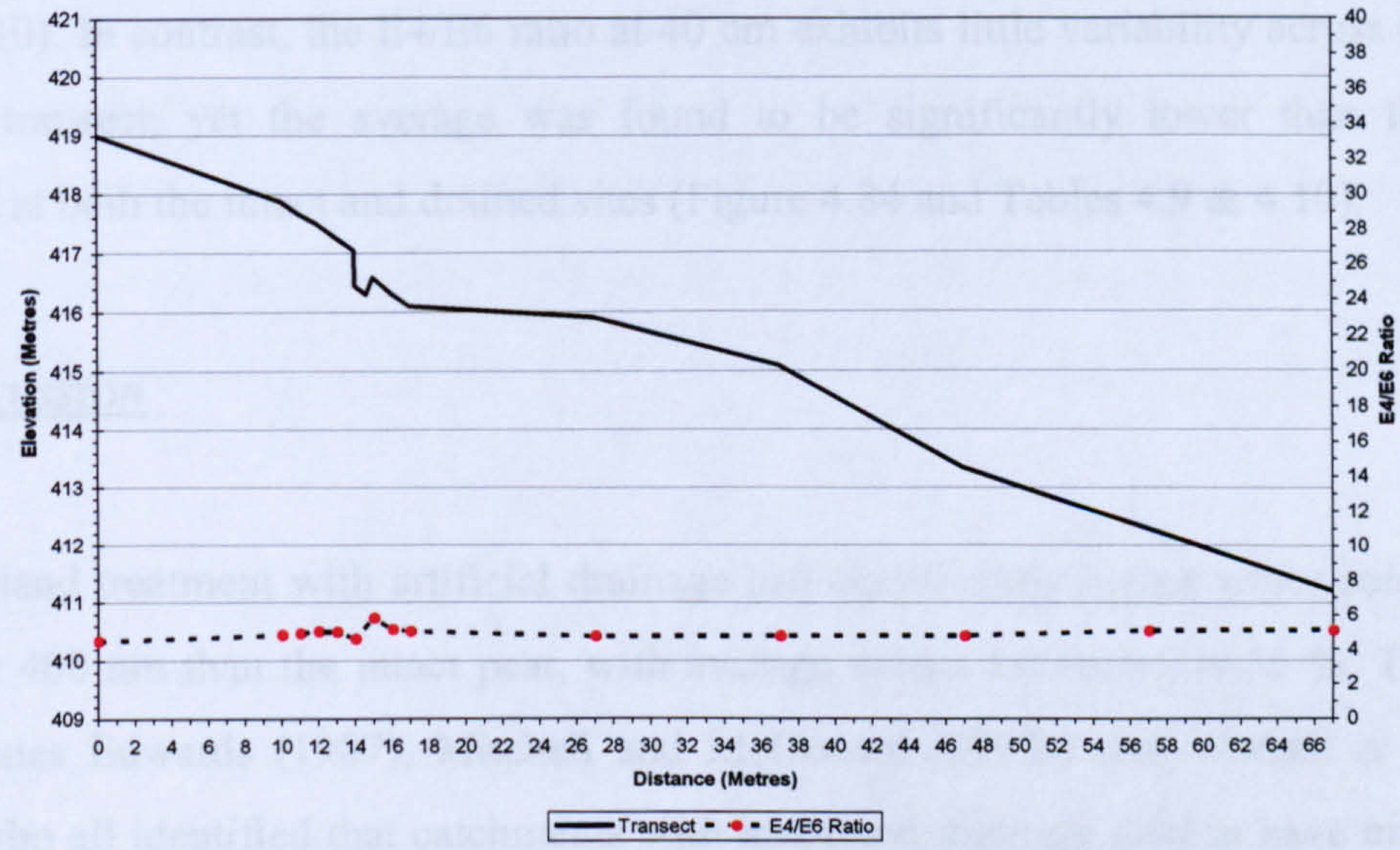


Figure 4.83 How the E4/E6 ratio at 40cm varies across the drained transect. Vertical bars represent the SE mean.

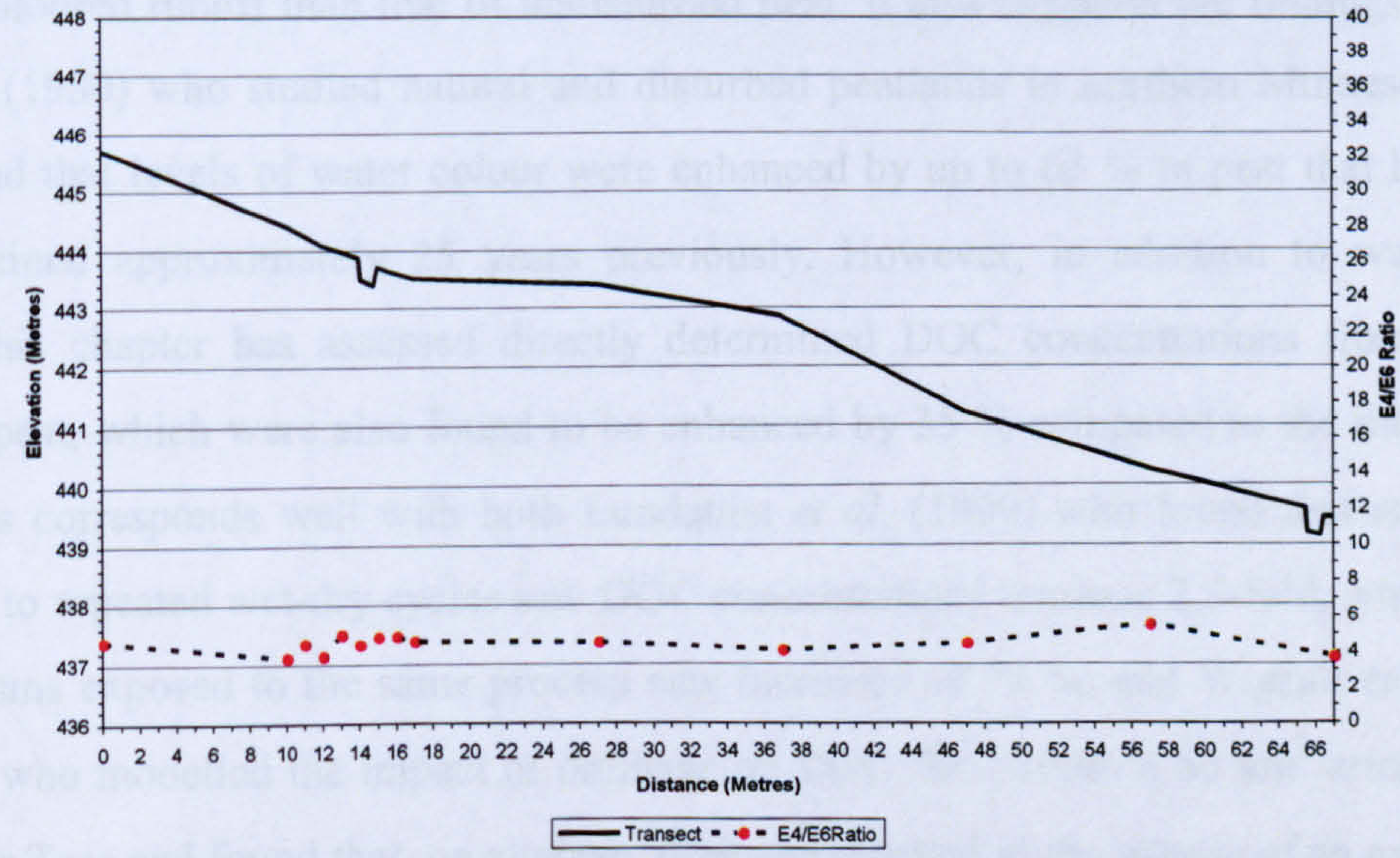


Figure 4.84 How the E4/E6 ratio at 40cm varies across the blocked transect. Vertical bars represent the SE mean.

The C/C and E4/E6 ratios appear to be relatively stable across the intact transect at 40 cm (Figures 4.79 & 4.82). At the drained site however, Figure 4.80 shows the C/C ratio appears to be slightly enhanced in the area immediately surrounding the ditch, which corresponds well with the significantly (p <0.001) higher average observed at this depth compared to the intact site (Tables 4.8 & 4.10). In contrast, although the E4/E6 ratio appears relatively stable across the drained transect, the mean value was found to be significantly lower than that of the intact site (Figure 4.83, and Tables 4.9 & 4.10). It can be seen in Figure 4.81 that the C/C ratio at the blocked site is more variable than that observed for the intact treatment at 40 cm, with values appearing slightly reduced up-slope of the ditch whilst down-slope they seem elevated, which results in a significantly (p <0.001) higher average relative to the intact site (Tables 4.8 & 4.10). In contrast, the E4/E6 ratio at 40 cm exhibits little variability across the blocked transect, yet the average was found to be significantly lower than that observed at both the intact and drained sites (Figure 4.84 and Tables 4.9 & 4.10).

4.4. DISCUSSION

The peatland treatment with artificial drainage had significantly higher water colour values at 400 nm than the intact peat, with average values enhanced by 35 %. This corroborates Edwards (1987), Mitchell and McDonald (1992a) and Worrall *et al.* (2003) who all identified that catchments with moorland drainage tend to have more highly coloured runoff than that of undisturbed peat. It also supports the findings of Clausen (1980) who studied natural and disturbed peatlands in northern Minnesota and found that levels of water colour were enhanced by up to 63 % in peat that had been drained approximately 25 years previously. However, in addition to water colour this chapter has assessed directly determined DOC concentrations from a drained peat, which were also found to be enhanced by 35 % compared to the intact site. This corresponds well with both Lundquist *et al.* (1999) who found that soils exposed to repeated wet-dry cycles saw DOC concentrations increase 2.5-fold, whilst microcosms exposed to the same process saw increases of 70 %; and Worrall *et al.* (2007b) who modelled the impact of drainage on DOC flux within a 60 km^2 area of the upper Tees and found that, on average, drainage resulted in the release of an extra 6.1 Kt C/year. Consequently, the installation of drainage ditches in blanket peat soils has been found to be highly influential in the release of DOC and discoloured waters, and is thus detrimental both to the sustainability of an important terrestrial carbon store and in the maintenance of inland waters of "good ecological status", as required by the EU Water Framework Directive.

Water samples extracted from the drain-blocked treatment showed this to be a highly successful strategy for improving carbon storage potential in a drained blanket peat, with the average DOC and colour values at the blocked site being reduced by 49 and 32 % compared to the drained site. This supports the findings of Worrall *et al.* (2007b) who modelled the impact of drain blocking on DOC release from a drained catchment, and predicted that for drains that had been blocked the average DOC flux would be 5.7 Kt C/year lower than an area where the drains remained open. In contrast, however, it goes against Worrall *et al.* (2007a) who observed that water flowing from drains that had been blocked 10 months previously had significantly higher DOC and colour values compared to unblocked drains, although no discernable change in stream characteristics were observed on the catchment-scale in their study.

Nevertheless, this may just be indicative of the fact that there may be different responses in the short and long-term to drain blocking and that although in the long-term it may be successful, the immediate effect may be to produce a flush of DOC/colour similar to that observed in the autumn after a summer drought. For example, after the initial flush of DOC in response to water table restoration and the subsequent enhanced mobility of labile products, concentrations are likely to decrease due to a reduction in the content of potential DOC in the remaining peat, because DOC release depends on soil organic matter content and if the soil layers have been degraded in any way, there is less available organic matter to produce DOC (Kalbitz & Geyer 2002). Such a loss of potential organic matter in the long-term (6 years) is evident when the DOC and colour values of the blocked treatment are compared to the intact site, as they are reduced by 31 % and 9 % respectively. Furthermore, the C/C ratio showed that for every carbon unit (e.g. per mg of C), the DOC at this treatment contained significantly more colour than per unit of carbon at the intact or drained sites, whilst the lower E4/E6 ratio suggests that older, more humified material is being sourced compared to the intact site, which all suggests that blanket peatland restoration involves a process of store exhaustion.

Analysis of the temporal variability in DOC and colour and the C/C and E4/E6 ratios shows that the differences identified between the sites was sustained throughout the sample period (January to November 2005). At all sites, peak DOC and colour values were observed during the late summer/early autumn, whereas the lowest values were recorded in late autumn/early winter, which corresponds to the autumn flush that is often reported in peat research (e.g. Naden & McDonald 1989). In contrast, the C/C ratio appears to peak in the late autumn/early winter, which suggests that although lower DOC and colour values are observed during this time the DOC actually contains more colour per carbon unit than that released during the summer months. Meanwhile, the E4/E6 ratio appears relatively stable at the drained and blocked sites through time, whilst at the intact site it is consistently higher and more variable, and exhibits a significant reduction during the summer months. This suggests that during times of enhanced DOC and colour production at the intact site, the organic matter is sourced from older, more humified peat, potentially that which is exposed during water table drawdown during the drier summer months. At the drained and blocked sites however, the E4/E6 ratio is probably lower and less variable because the associated water table disturbance has already altered the source of DOC and exposed deeper peat layers. For example, at the blocked site the combination of the high C/C and low E4/E6 ratios suggests that the DOC is obtained from a more humified source that is dominated by larger, more darkly coloured humic rather than fulvic acids compared to the intact site. This implies that the disturbance associated with drainage and drain blocking results in some form of alteration to the source of DOC and therefore to production and/or transportation processes operating within the peat, such as sustained microbial activity at depth or modified hydrological routing through the soil profile.

In order to further comprehend the likelihood of such mechanisms, it was necessary to assess how the composition of DOC varied at depth across the three treatments. At the intact site, although there was a trend towards increased DOC and colour with depth, analysis of the C/C and E4/E6 ratios indicated that the peat can be divided into two distinct layers; an upper layer consisting of depths 0 to 10 cm, and a lower layer comprising depths 20 to 40 cm. In the upper layer, the E4/E6 and C/C ratios are significantly higher than the lower layer. This suggests that the upper layer is dominated by immature fulvic acids (from the newly decomposing plant litter), in which there is a relatively high level of microbial activity. Meanwhile, the reduced ratios in the lower layer imply that more mature, darkly coloured, humic acids and a reduced level of microbial activity dominate this part of the peat mass. The lack of activity and accumulation of humified organic matter in this lower layer suggests that this area is anoxic, which would imply that the water table does not normally exceed 10 cm depth in the intact peat. The properties of the two layers identified here align with the traditional two-layered model of blanket peats, which consist of an upper peat layer known as the acrotelm in which water table fluctuations occur and a lower catotelm layer that is permanently saturated (Holden & Burt 2003b; Ingram 1978; 1983).

At the drained site, there was a spike in data at 20 cm depth where DOC and colour values were significantly higher than at other depths. When the intact and drained sites were compared, there were no significant differences in the DOC or colour values in overland flow or at 5 cm depth. At 20 cm however, the DOC and colour values were 60 % and 146 % (respectively) greater than the same layer of intact peat. This suggests that the greatest area of influence in elevating DOC and colour values at the drained site occurs at or around 20 cm depth. Assessment of the C/C and E4/E6 ratios at depth support this finding and suggest that the spike in DOC and colour values at 20 cm is the result of an increased level of production due to a modification of the peat in response to a lowered water table. For example, the characteristics of the acrotelm layer (as determined by C/C and E4/E6 data for the intact site within the upper 10 cm) are apparent in the drained peat at 20 cm, as significant reductions in the C/C and E4/E6 ratios are not evident at this site until depths >20 cm (i.e. 40 cm). The apparent lowering of the acrotelm base from 10 to 20 cm depth would suggest that a greater proportion of the soil body has been oxidised in response to a lowering of the water table. This, in conjunction with increased DOC and colour at 20 cm in the drained peat, suggests that there has been a stimulation of microbial activity at this depth. Thus, although carbon stored within the deeper anaerobic peat layers is not normally a major source of DOC, it does represent a significant potential carbon source that could be mobilised by water table drawdown. For example, Freeman *et al.*

(2001b) observed that intact peatlands typically exhibit low biodegradation rates, and thus low DOC release, because the anaerobic conditions constrain the activity of the enzyme phenol oxidase allowing the accumulation of phenolic compounds, which severely restricts the activity of pivotal degrading hydrolase enzymes. However, when the water table is lowered and the peat is oxygenated they found that the level of phenol oxidase increased significantly, which reduced the concentration of organic phenolic compounds meaning that the hydrolase enzymes could freely breakdown the organic material. In addition, Schiff *et al.* (1998) showed that maximum decay rates occur around the position where the water table fluctuates the most, rather than in the fully aerobic zone, due to the specialist microbial communities that inhabit this zone.

At the blocked site, even though the values are significantly lower than the two other treatments, there is still a pattern of increasing DOC and colour with depth. However, standing out from this overall pattern are the values from 10 cm depth, which are significantly lower than those at all other depths in this treatment. The pattern of C/C and E4/E6 ratios at depth for the blocked site appear to suggest that the lower DOC and colour values, particularly those at 10 cm depth, may be the result of a flushing and subsequent modification of soil layers in response to a rising water table. For example, there was a significant reduction in the E4/E6 ratio between 10 and 20 cm depth, indicating that the base of the acrotelm had been raised in the blocked site to depths <10 cm, indicative of successful water table restoration. Schiff *et al.* (1998) suggested that above the maximum depth of the water table, the water flow is rapid enough to flush out DOC produced in surface layers, and that within the catotelm the DOC production may be occurring at lower rates, but, as the groundwater flow is much slower DOC could still accumulate. Schiff *et al.* (1998) concluded that the concentration maximum therefore does not represent a maximum in production in most cases, but the depth of highest accumulation.

The apparent 'flushing' of DOC and colour in the upper (<10 cm) peat layer, whereby values are significantly lower than those at 20 or 40 cm, in addition to the significant reduction in the E4/E6 ratio between 10 and 20 cm, suggest the maximum water table depth may have been successfully restored at the blocked site. However, the C/C ratio actually remains significantly higher in the lower layer (>10 cm) than the upper layer (<10 cm), which in conjunction with the elevated DOC and colour values at such depths, suggests there may be enhanced microbial activity and internal cycling of existing organic matter. This corroborates with Freeman *et al.* (2001b) who suggested that the reduction in the concentration of phenolic compounds in response to the preceding oxygenation allows decomposition of organic matter to continue at depth by hydrolase enzymes, even after the water table has been restored.

To further determine the influence of the hydrological re-routing and altered enzyme activity mechanisms at the drained and blocked sites it was necessary to assess the variability in DOC and colour values across the transects located along each hillslope. At the drained site, DOC and colour values were generally enhanced in the up-slope direction from the ditch. For example, enhanced DOC and colour values in OLF samples up-slope suggest a greater amount of rainfall/runoff is being drawn down into, and is mixing well with, the soil and its porewaters before it re-emerges at the surface as return flow. This is likely to be caused by a more dynamic/fluctuating water table at this point enabling enhanced labile carbon production, which is then flushed out of the soil as return flow when the water table rises. This is supported by data collected from within the soil body where elevated DOC and colour values are also found up-slope of the ditch, with elevated C/C ratios at this point suggesting this was in response to enhanced levels of microbial activity.

In contrast, reduced DOC and colour values were observed in OLF in the few metres surrounding and down-slope of the ditch at the drained site, which suggests a greater volume of runoff travelling over the surface at this point is being drawn down into the soil, rather than being "pushed" out as return flow, in response to a continually lowered water table and de-saturation in the upper soil layers. DOC and colour were also reduced within the soil body in this area, which in addition to a reduction in the C/C ratio suggests this may be the result of a lowered level of microbial activity and therefore DOC production. However, the reduction in DOC and colour may also be the result of a lowered water table causing a flushing effect that results in more water being drawn down into the soil. This means more DOC/colour would be transported to the deeper soil layers either by enhanced through flow or via the development of macropores, which may account for the heightened levels at depth compared to the intact site.

A similar pattern of elevation in the up-slope direction and reduction immediately surrounding and down-slope of the ditch is observed at the blocked treatment. However, the average DOC and colour values were greatly reduced compared to the drained site. This suggests that the trend observed along the blocked transect is more likely to be a relic of the conditions existing before the ditch was blocked, and that subsequently a raised yet highly fluctuating water table has either flushed out organic material and/or reduced the level of labile carbon production. For example, the greatly reduced DOC concentration, especially in the area nearest the ditch, suggests that a rising water table in combination with a build up of water in the reservoir behind the peat dam may have caused a significant flushing of porewaters. Furthermore, there may be a reduction in DOC productivity rates as the C/C ratio is significantly lower in the down-slope direction, indicating there may be reduced microbial activity.

Differences in the concentration and flux of DOC reflect the relative rates of DOC production, sorption and consumption, as well as changes to the pathways through which water transports it. Furthermore, the type of substrate utilised, especially with respect to its chemical composition and degree of decomposition, influences the rate of DOC production with smaller amounts of DOC released from better decomposed materials (Moore & Dalva 2001). The average C/C ratio for the blocked treatment was found to be significantly higher than both the intact and drained sites. This indicates that there may be altered levels of microbial activity/DOC productivity within the peat layers at the blocked site, particularly at depth given that significant increases in the ratio are only seen at 20cm and 40cm compared to the intact site. This is because coloured humic substances are normally considered to be more recalcitrant towards microbial degradation than the uncoloured non-humic fraction, and thus variations in the C/C ratio are thought to relate to changes in soil decomposition processes (Alkan *et al.* 2007; Scott *et al.* 1998). It is thought the re-saturation of the peat layers in response to peatland restoration and a rising water table may have caused a flushing of porewaters that resulted in DOC becoming limited in supply. This may have then initiated a process of store exhaustion whereby microbes act to continually breakdown existing organic material rather than newly sourced matter, and so work not only to change the concentration of DOC but also its composition. For example, Waddington and Price (2000) found that high rates of decomposition generally result in a lower proportion of readily available organic carbon combined with the accumulation of recalcitrant humic compounds, and Raymond and Bauer (2001) found that young DOC can be selectively degraded, leaving an older and more refractory component. Thus, it appears that the low DOC and colour values, yet high C/C ratio are characteristic of a more humified peat, whose labile carbon compounds had been consumed over time by microbes. This is supported by the significantly lower E4/E6 ratio at the blocked site compared to the intact site, which suggests the DOC in the porewaters is more aged and "processed" as it is dominated by mature, darkly coloured humic material rather than the immature lighter-coloured fulvic material seen at the intact site. Furthermore, a reduction in DOC production may be due to the accumulation of compounds unfavourable to microbial activity such as lignins, phenolics and humic substances (Hogg *et al.* 1992).

The heightened C/C ratio at the blocked site may also be the result of the preferential removal of the smaller, uncoloured non-humic portion of DOC compared to the larger, coloured and more resistant humic material, in response to a rising water table. This is because DOC can be stored in the soil until the peat is rewetted, after which a large flush of material occurs (e.g. the autumn flush), and the store of DOC becomes much depleted, especially in the more labile hydrophilic fraction, with soil waters subsequently becoming dominated by the refractory hydrophobic fraction (Scott *et al.* 1998). For example, Jardine *et al.* (1990b) assessed the subsurface transport of DOC and found that hydrophilic DOC is preferentially channelled through the soil relative to hydrophobic DOC, which is more strongly adsorbed by the soil.

Organic matter input quality is a determinant of DOC reactivity and consequently THM production potential and is usually divided into two major classes: hydrophobic and hydrophilic organic matter (Fleck *et al.* 2004). The hydrophobic acid fraction typically consists of high molecular weight compounds, such as aliphatic carboxylic acids, aromatic carboxylic acids, phenols, and aquatic humic and fulvic substances, resulting in a relatively low level of solubility compared to the hydrophilic fraction (Freese *et al.* 2001; Izbicki *et al.* 2004). In contrast, the hydrophilic acids typically consist of more readily soluble compounds and may contain sugar acids, alcohols, polyfunctional organic acids, and aliphatic acids with five or fewer carbon atoms (Thurman 1985). Therefore, hydrophobic compounds are generally easier to treat at the water works than the hydrophilic components (Banks 2006). Furthermore, the humic acid fraction of hydrophobic organic matter is highly reactive and therefore more readily removed by coagulation, than the fulvic acid fraction (Freese *et al.* 2001). Unfortunately however, there currently is not an easy test that can be carried out to fractionate the water into hydrophobic and hydrophilic acids as tens of litres of sample are required. Consequently, measurements of SUVA at 254nm are used as a surrogate for THM production potential, as the aromatic rings and double bonds in the humic acid structure absorb highly at this wavelength, and thus SUVA gives an indication of the ratio of hydrophobic to hydrophilic acids in the water (Banks 2006). Under the same principles, the C/C ratio may also be used to indicate the ratio of hydrophobic to hydrophilic acids in the water (Banks 2006). Thus, as the SUVA or C/C ratio increases, the hydrophobicity of the water is likely to increase, i.e. of the total amount of DOC, a greater proportion is hydrophobic.

There is concern that changes in upland land management could change the DOC from a predominantly hydrophobic mixture, which can be removed by Ferric coagulation, to a hydrophilic mixture, which is less easily removed and would bring major problems at the water treatment works. It was found that although the installation of drainage ditches significantly enhances the release of discoloured water, there is no difference in the C/C ratio when compared to the intact site. This is good news in the sense that peatland drainage does not appear to alter the hydrophobic/hydrophilic ratio and thus DOC can be removed relatively easily by coagulation and avoids THM formation during chlorination. However, it is bad news in the sense that it generally means a much higher concentration of coagulant is needed to remove the DOC, which could prove costly for the water industry. In contrast, not only does blocking appear to reduce the level of water discolouration, it is also likely to improve the treatability of catchment waters given that blocked soil waters exhibit i) a higher C/C ratio, which suggests it contains a greater proportion of coloured hydrophobic acids; and ii) a lower E4/E6 ratio, meaning the hydrophobic fraction is dominated by more humic acids, meaning DOC can be easily removed using acidification and coagulation techniques.

4.5. CONCLUSIONS

The artificial drainage of blanket peat significantly increases the DOC concentration and level of water discolouration in soil water solutions by an average of 35 % compared to un-drained peat. Most of the additional DOC and colour produced appears to come from peat deeper than 10 cm but shallower than 40 cm depth, with observed values at 20 cm enhanced by 60 % and 146 % respectively, compared to the intact treatment. Assessment of the C/C and E4/E6 ratios shows significant deviation from the intact site, specifically at a depth of 20 cm, suggesting that the increased DOC and colour values occur in response to modified DOC production and/or transportation processes operating within the peat, such as enhanced microbial activity via oxygenation from a lowered water table. Consequently, the installation of drainage ditches in blanket peat ecosystems was found to be highly detrimental, both to the sustainability of an important terrestrial carbon store and in the maintenance of ecologically sound upland water resources.

The drain-blocked treatment saw average DOC concentrations and water colour values successfully reduced by 49 % and 32 % respectively, compared with the drained site. Furthermore, DOC and colour values at the blocked treatment were found to be significantly lower than those at the intact site, especially at a depth of 10 cm, which suggests a process of store exhaustion and flushing operates in response to a rising water table. The E4/E6 ratio was significantly lower at both the drained and blocked treatments compared with the intact site, which suggests that the disturbance and water table drawdown associated with these changes in land management alters not only the concentration of DOC, but also its source and composition. The DOC at the intact site appears to be produced from relatively young, labile fulvic material, whilst that of the drained and blocked sites is supplied from older, more humified organic matter that is dominated by refractory humic compounds. The C/C ratio was higher at the blocked site than either the intact or drained treatments, which suggests there may be continued disturbance to DOC production and/or transportation processes even after restoration; processes such as sustained microbial activity and internal cycling of existing organic matter, or the preferential removal of labile DOC fractions in response to pore water flushing associated with a rising water table.

Differences in the carbon source, decomposition rate, transportation pathway, and carbon availability all have profound effects on the carbon forms that reach stream waters and are subsequently extracted for drinking water. Although the installation of drainage ditches significantly enhances the release of discoloured water, there was no difference in the C/C ratio when compared to the intact site. Thus, it appears the DOC released from drained catchments can still be removed using traditional techniques such as Ferric coagulation, although the higher DOC concentrations means a greater quantity of coagulant will be needed, which could prove costly. In contrast, drain blocking appears to improve the treatability of catchment waters, as soil-water solutions not only exhibited lower DOC concentrations and colour levels, but the DOC that was released contained a greater proportion of coloured hydrophobic acids, which means catchment waters can be easily treated using existing acidification and coagulation techniques. Therefore, drain blocking is recommended as a suitable technique for improving carbon storage potential and upland water quality in a blanket peat soil.

CHAPTER 5

SPATIAL AND TEMPORAL VARIABILITY IN THE COLOUR – CARBON RELATIONSHIP

5.1. INTRODUCTION

A strong linear relationship between DOC concentration and water colour is often reported from peatland waters, and as colour can be measured easily and at minimal expense, a colour – carbon relationship is often used to monitor and predict DOC flux based solely on water colour measurement (e.g. Dobbs *et al.* 1972; Mattson *et al.* 1974; Moore & Jackson 1989; Moore 1987; Tao 1998; 2005; 2004; Worrall *et al.* 2002; 2003; 2004). Typically, water colour is measured with a spectrophotometer that records the level of absorbance at 400 nm for a given path length, and a regression equation is produced relating a sample of absorption values to DOC concentrations for a peatland catchment. Often however, this regression is then used to predict DOC fluxes over long time periods within the catchment where a long-term water colour record exists (Worrall & Burt 2004; Worrall *et al.* 2002) or for additional catchments where DOC has never been recorded (2004).

The possibility of increasing DOC concentrations from UK peatland catchments was first observed by the elevated levels of water discolouration during the 1980s (e.g. McDonald *et al.* 1989), whilst longer-term data extends back into the 1960s, although it is generally limited to water colour records collected by water supply companies for peaty upland areas of northeast England (Watts *et al.* 2001; Worrall *et al.* 2003). Consequently, the systematic measurement and monitoring of DOC in UK upland waters, especially with regard to environmental change, has been relatively poorly recorded and is generally limited to a small number of sites, such as the Plynlimon catchment in north Wales and Moor House NNR in northern England. This is despite the fact that i) DOC is one of the simplest and most important determinations in organic geochemistry and which can be measured to within ± 0.1 mg C l^{-1} by processes such as oxidation to CO_2 in a combustion-infrared analyser (Clesceri *et al.* 1998); ii) DOC composition, and thus its spectral characteristics can be influenced by a wide range of biogeochemical and hydrological processes; and iii) as identified in Chapter 4, the ratio of coloured to un-coloured compounds in DOC (i.e. the C/C ratio) has been found to vary with depth and time in blanket peat soil waters, and also in response to changes in the type of land management undertaken.

If we are to determine the influence of environmental change on the fluvial carbon export from peatland catchments to lakes, reservoirs and the oceans with any degree of precision, it is extremely important that we are able to provide an accurate measure of the DOC flux transported in rivers and streams. It is therefore the aim of this chapter to assess the suitability of using spectrophotometric techniques to accurately monitor/predict DOC concentrations in upland blanket peat soil water solutions by determining whether the process modifications brought about by changes in blanket peat land management, such as drainage and drain blocking, influence the intrinsic relationship between DOC and water colour.

5.2. METHODS

In regression analysis, where an independent variable is used to predict the value of a dependent variable, there are often situations that arise in which data are observed for more than one group of subjects. For example, it is well known that the relationship between height and weight differs between the male and female gender categories. Thus, it is possible to possess more than one group of data and to have calculated a regression equation to describe the relationship for each set. If this is the case, it is then necessary to test whether the relationships are statistically different from one another to determine whether they warrant separate analysis, or whether they actually estimate the same population and thus would be better expressed using a common regression analysis.

When comparing regression lines, the overall hypothesis tested is that of coincidence. That is, to test whether the different relationships demonstrated between groups are in fact exactly the same. If coincidence is accepted, then a single overall regression line can be fitted to all of the data. However, if coincidence is rejected then there are differences in either the slope and/or intercept of one or more of the groups. To test for coincidence the first step is to check whether the slopes of the regression lines are significantly different. If the slopes are found to differ then it is assumed that different populations have been sampled as the lines do not coincide. However, if the population regression lines are not concluded to have different slopes, then the lines are only assumed to be parallel.

The second step is to determine whether the population regressions have the same elevation (i.e. the same intercept) and thus the lines coincide. For example, if the regression lines are found to be parallel, then the effect of the independent variable (in this case water colour) on the dependent variable (DOC) is the same in each group. However, the 'base-line' values may be different between the groups (i.e. the slopes are equal but the intercepts differ), and thus, a test for the equality of intercepts is also required. If the intercepts are not found to differ, this means that the base-line for the response variable is the same for each regression, even after accounting for the effect of the grouping variable, and if the slopes are identical between groups then the lines will coincide. However, if the intercepts are found to differ, then it can be concluded that the same predictor value in each group produces a different response value, and thus the lines are not coincident.

Figure 5.1 illustrates the possible outcomes of a comparison between two regression lines. Figure 5.1a shows that the two lines are completely different, both with regard to slope and intercept; Figure 5.1b shows the two lines are parallel, as although the slopes are equal the intercepts differ; Figure 5.1c shows that the intercepts of the two lines are equal but the slopes differ; and Figure 5.1d shows that the two lines coincide as both the slope and intercept are equal. If it is concluded that the separate regression lines have different intercepts and/or slopes, then separate regression equations are required. However, if it is found that neither the slope or intercept differ, then a single regression equation comprising a common regression coefficient and a common intercept should be used.

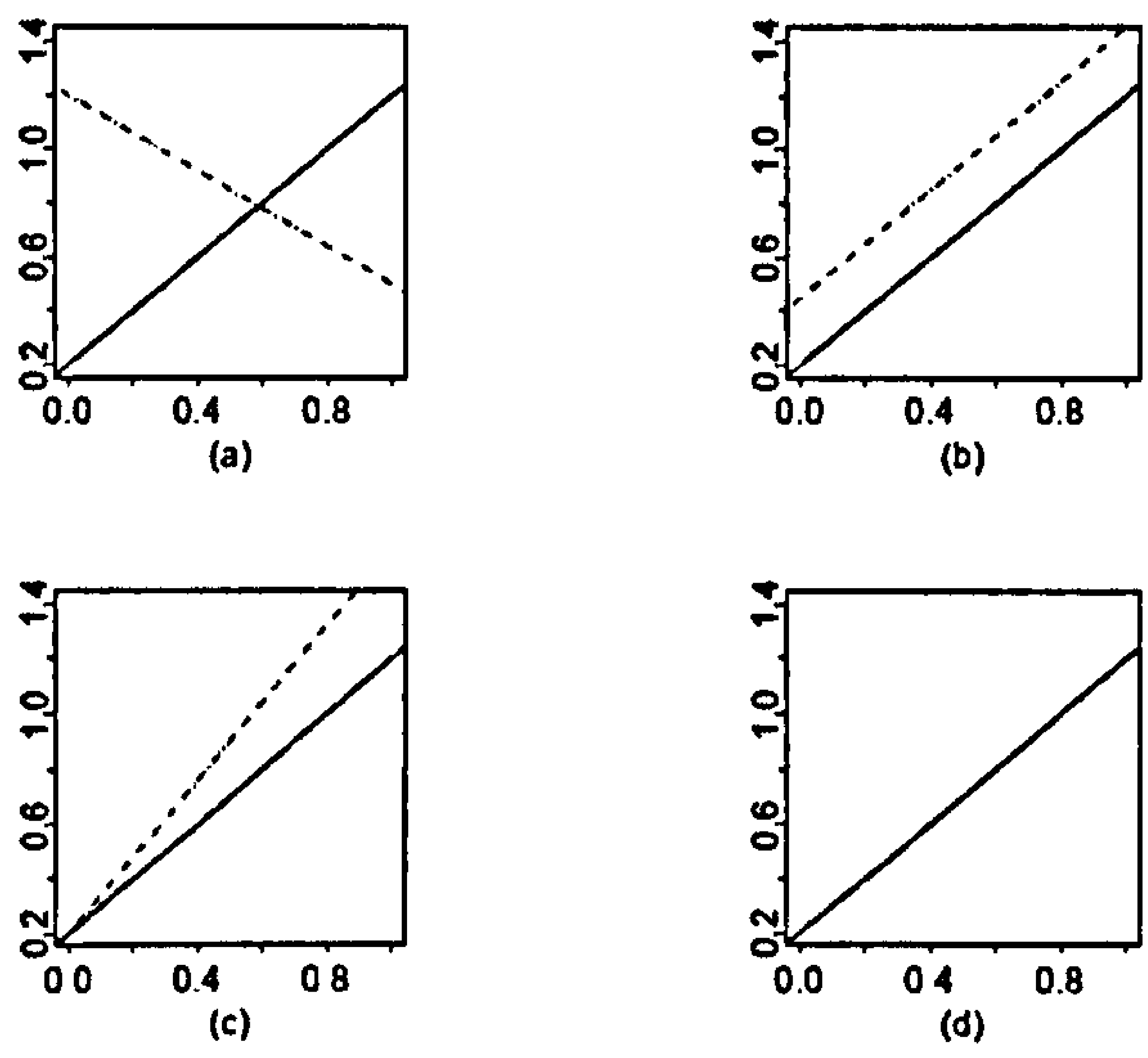


Figure 5.1 The possible outcomes of comparing two regression lines, sourced from Larsen (2006).

The data investigated consisted of a total of 1,047 paired DOC and colour (Abs^{400}) soil water samples taken from the three sites located within the Oughtershaw Beck catchment, which were collected using the sampling regime and protocols described in Sections 3.3 and 4.2. Correlations between the two variables were performed using Spearman Rank, whilst analysis of covariance (ANCOVA) was used to compare the slope and intercepts of individual regression lines in order to assess whether there was any significant variation in the colour – carbon relationship between groups.

5.3. RESULTS

Table 5.1 shows that the pooled dataset of 1,047 samples, taken from all three sites has a significant (p <0.001) and strongly positive (0.88) correlation between DOC and colour. However, the relatively large range in residual values indicate that the regression model encounters a fair amount of error in predicting some DOC concentrations. In addition, although there is a strong relationship between DOC and colour it can be seen in Figure 5.2a that the spread of the pooled data across the regression line appears to increase with elevated values, suggesting the assumption of homoscedasticity required for reliable regression analysis may have been violated. Consequently, residual analysis was undertaken for the pooled data; this showed that although the errors associated with the model are relatively normally distributed (Figure 5.3), there is an apparent fan-like pattern when the standardised residuals are plotted against the standardised predicted values (Figure 5.4). This increasing level of variance across the residuals implies that the model has indeed encountered heteroscedasticity, which limits the validity of the pooled data regression in this instance.

Following this, the pooled data was broken down in to sub-groups for site-specific analysis. Figure 5.2b clearly shows there are deviations between the resultant three regression lines, which indicates that the colour – carbon relationship may vary in response to the type of land management undertaken. In addition, the site-specific regressions appear to reduce the spread of data across each line suggesting that this method of analysis may be better at explaining the variance in the data. Evidently, in Table 5.1 it can be seen that the site-specific analysis generally improved the fit of the regression models, with the R^2 and correlation values increasing in two out of three cases, and reduced the magnitude of error, with the range in residual values falling by 28 % from 85.64 in the pooled data to an average of 61.66 for the site-specific data. However, although Figures 5.5 – 5.7 indicate that the distribution of the residuals for the three sites appears to be relatively normal, the residual plots presented in Figures 5.8 – 5.10 show that only the data from the drained site seems to fulfil the assumption of homoscedascity, as a fan-like spread of the residuals is still evident at the intact and blocked sites.

	Min Residual*	**Max Residual***	**Correlation#**	**R^2**	**n**
Pooled +	-42.29	43.35	0.88	77 %	1047
Site-specific • – Intact	-27.72	37.88	0.87	76 %	457
Site-specific • – Drained	-22.27	36.99	0.89	80 %	208
Site-specific • – Blocked	-21.13	38.98	0.93	86 %	382

* = The residual of the error term, i.e. the minimum and maximum differences between predicted DOC and actual DOC.

= Spearman rank correlation, all significant at $p = 0.01$.

+ = DOC values are predicted from Abs^{400} data using a "pooled" regression equation that was created from the paired DOC-Abs^{400} samples collected from all three sites.

• = DOC values are predicted from Abs^{400} data collected from an individual site using a "site-specific" regression equation that was created using only the paired DOC-Abs^{400} samples collected from the specific site under investigation.

Table 5.1 Correlation and regression statistics for pooled and site-specific analysis.

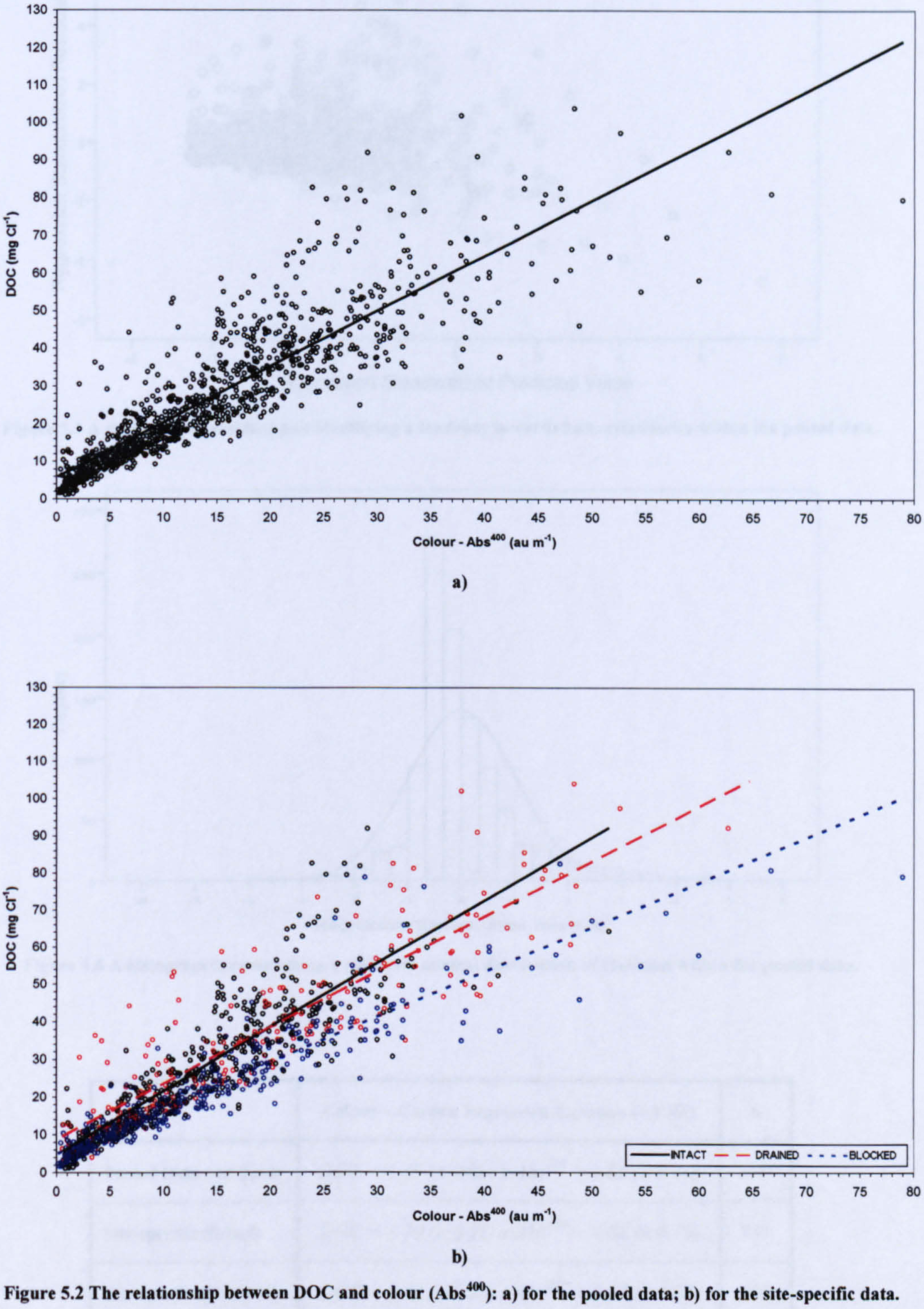


Figure 5.2 The relationship between DOC and colour (Abs^{400}): a) for the pooled data; b) for the site-specific data.

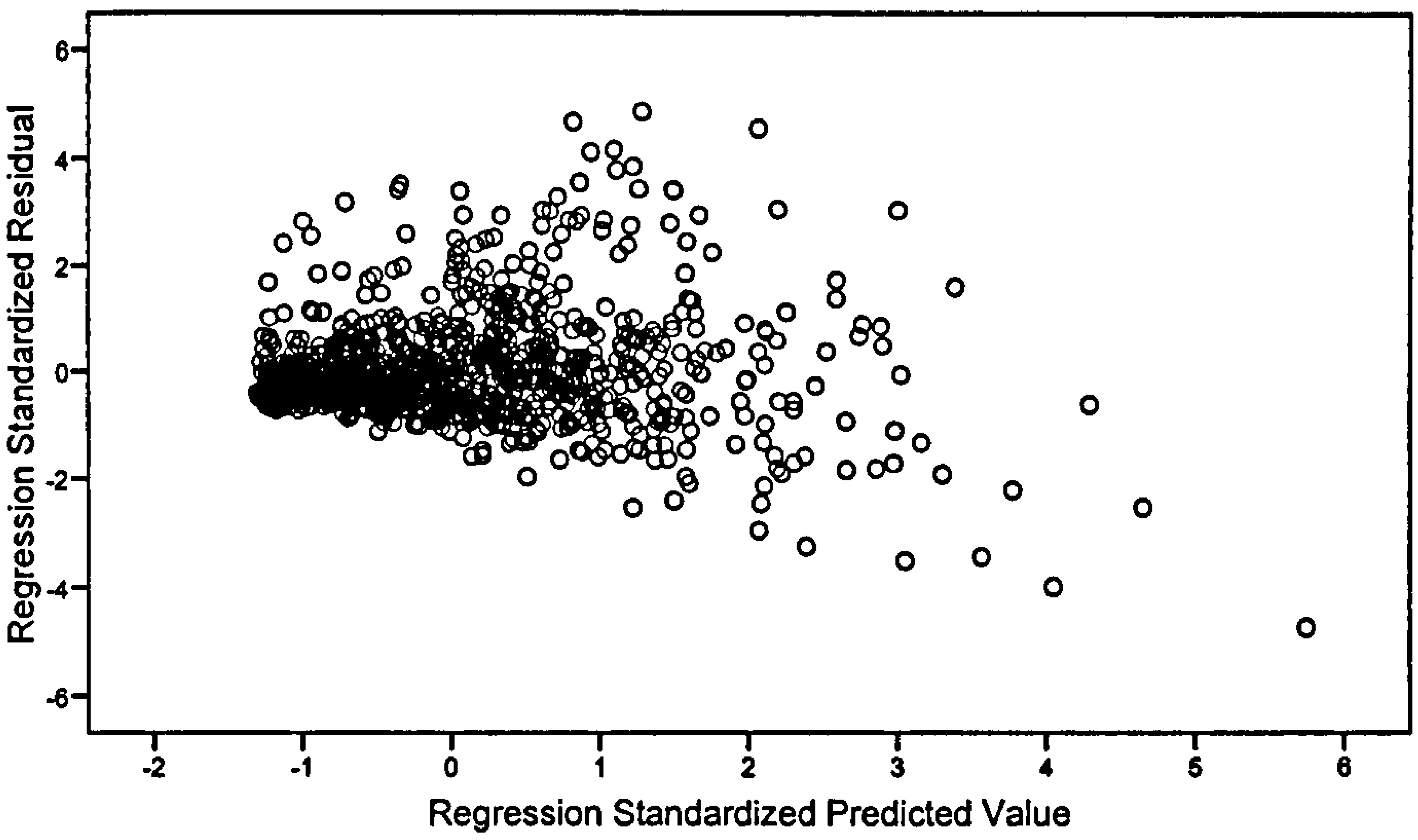


Figure 5.3 A standardised residual plot identifying a tendency towards heteroscedascity within the pooled data.

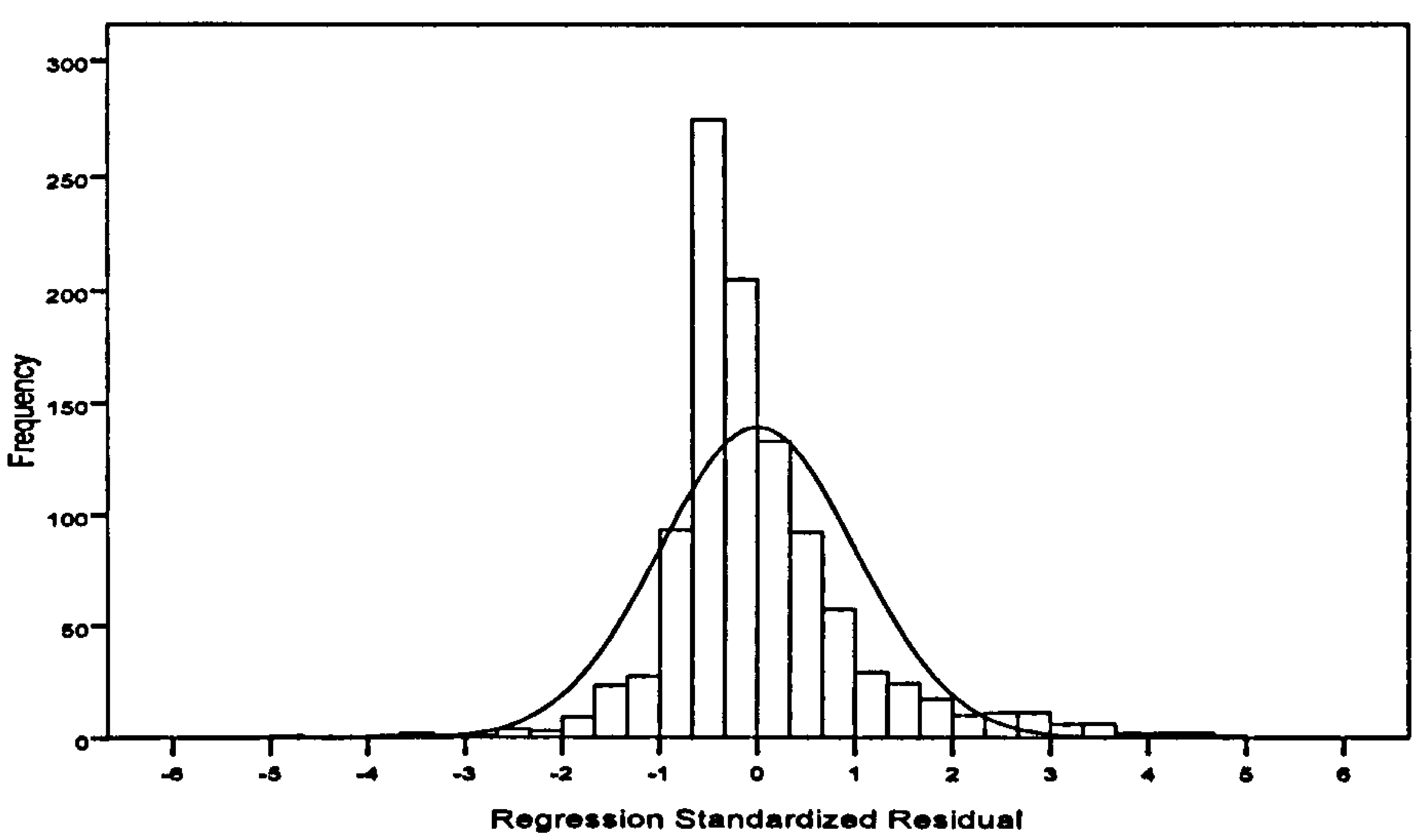


Figure 5.4 A histogram demonstrating a relatively normal distribution of residuals within the pooled data.

	Colour – Carbon Regression Equation (± 1 SE)	n
Pooled Data (All Sites)	$DOC = 1.47\ (\pm 0.03) \times Abs^{400} + 5.82\ (\pm 0.46)$	1047
Site-specific (Intact)	$DOC = 1.70\ (\pm 0.05) \times Abs^{400} + 4.68\ (\pm 0.75)$	457
Site-specific (Drained)	$DOC = 1.49\ (\pm 0.05) \times Abs^{400} + 8.74\ (\pm 1.22)$	208
Site-specific (Blocked)	$DOC = 1.21\ (\pm 0.03) \times Abs^{400} + 4.96\ (\pm 0.45)$	382

Table 5.2 Pooled data and site-specific regression equations.

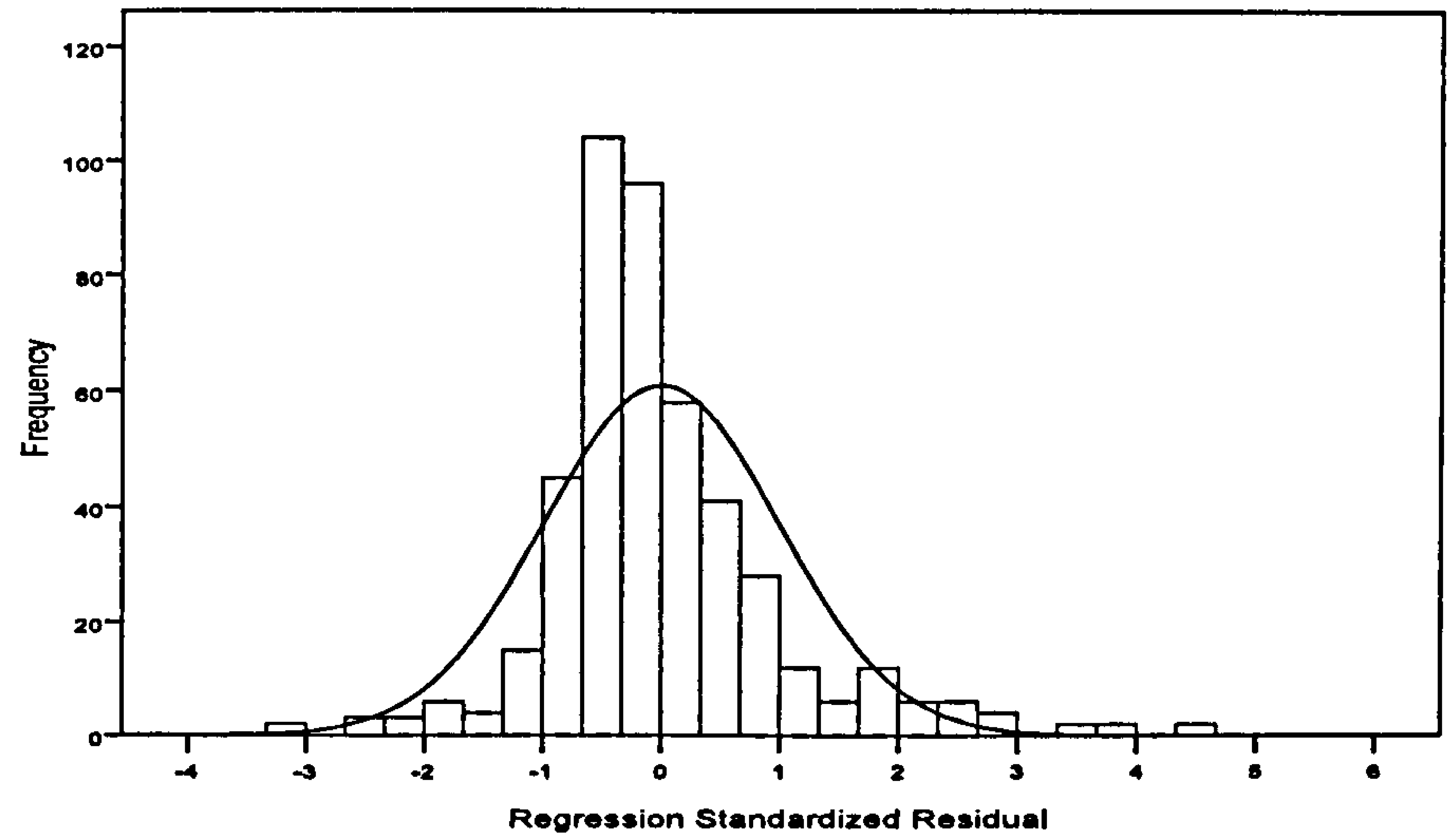


Figure 5.5 A histogram demonstrating a relatively normal distribution of residuals within the intact data.

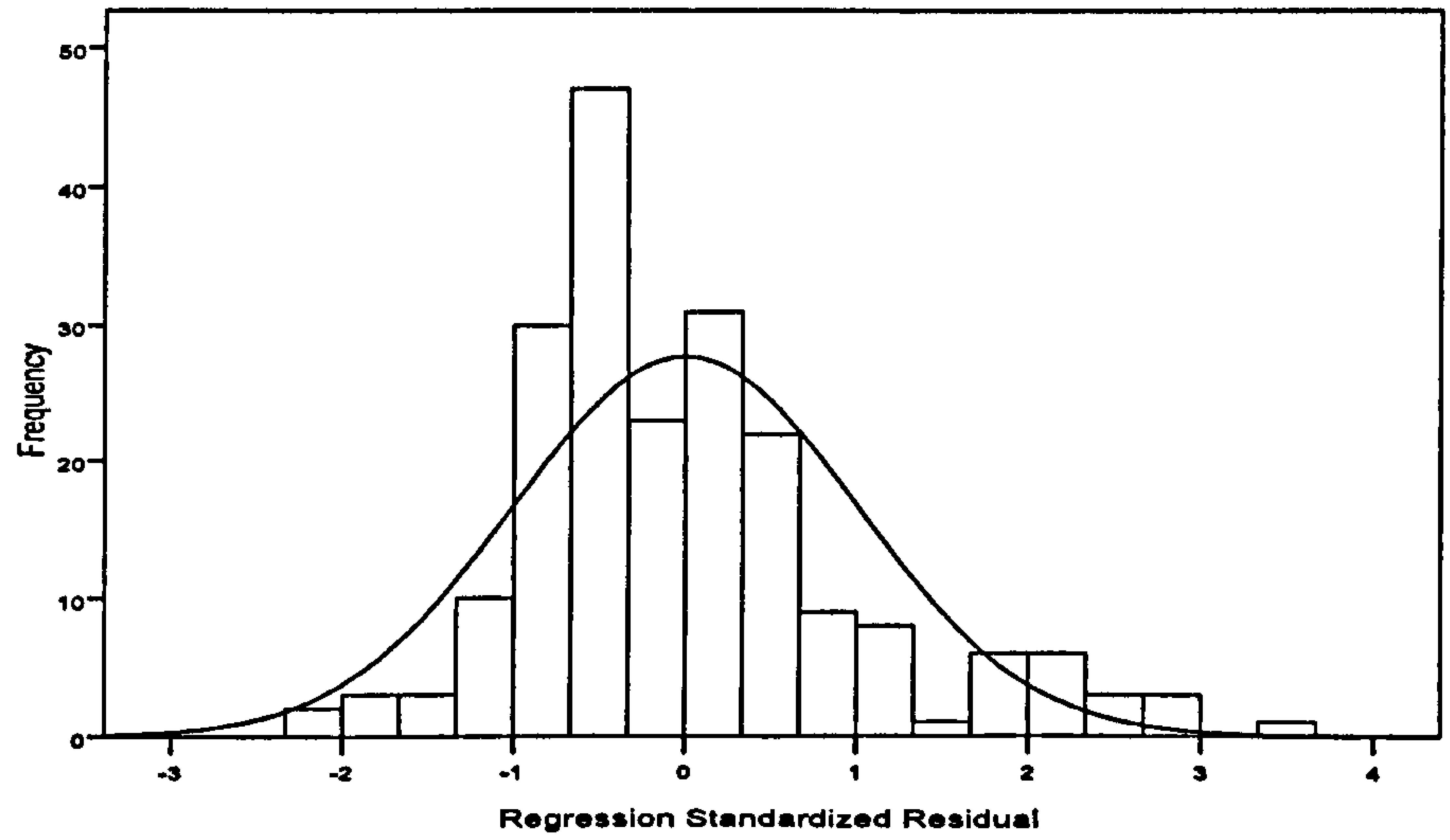


Figure 5.6 A histogram demonstrating a relatively normal distribution of residuals within the drained data.

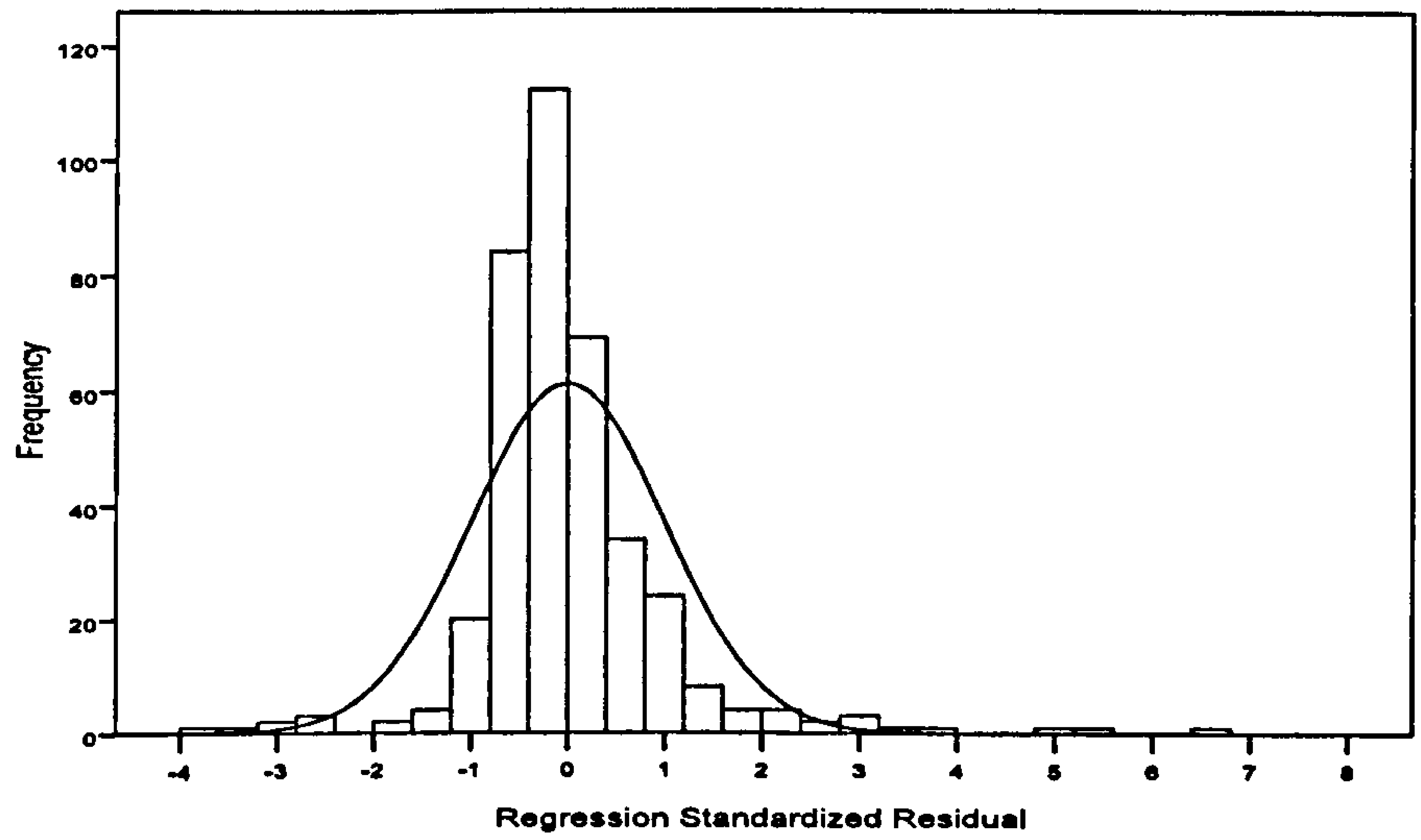


Figure 5.7 A histogram demonstrating a relatively normal distribution of residuals within the blocked data.

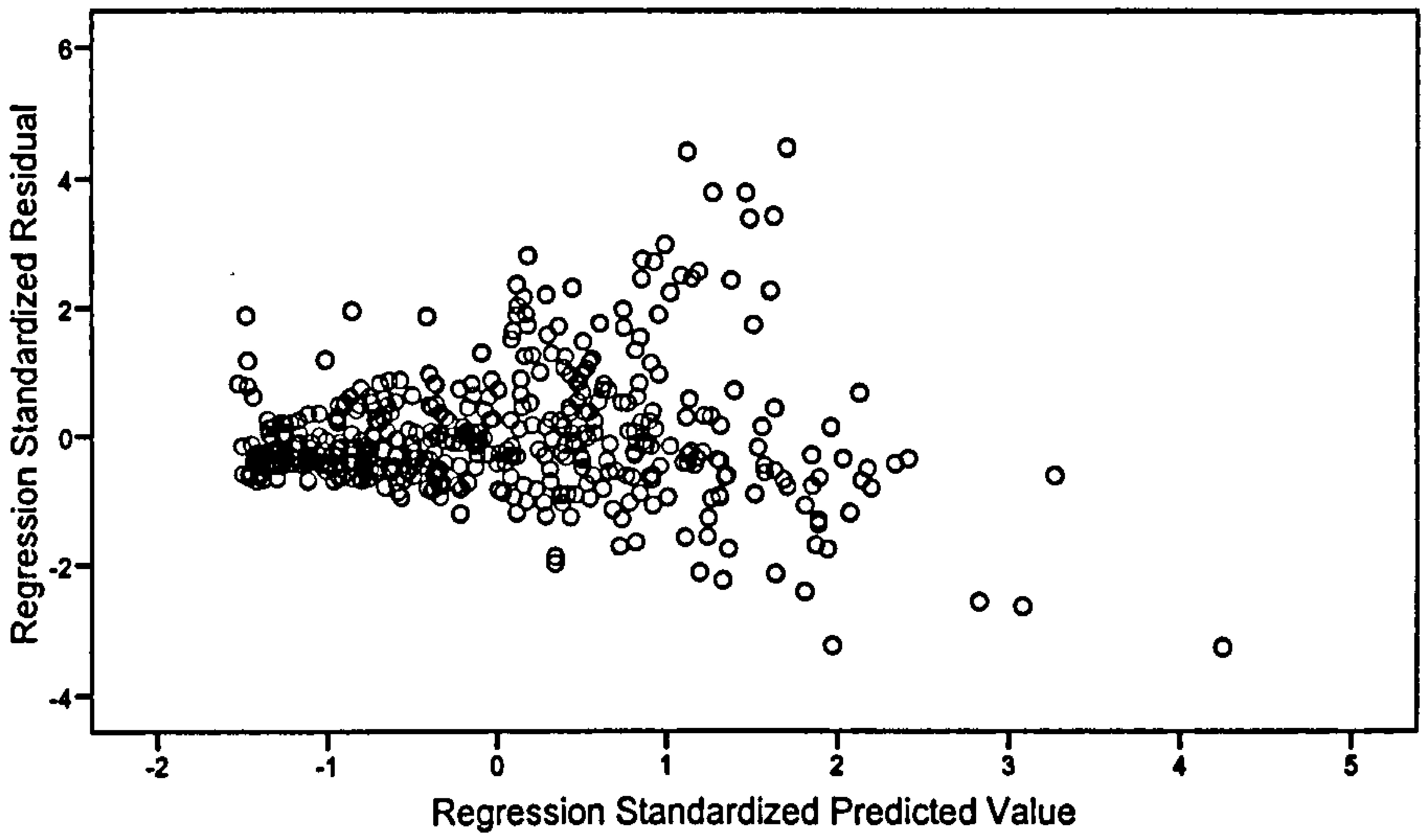


Figure 5.8 A standardised residual plot identifying a tendency towards heteroscedascity within the intact data.

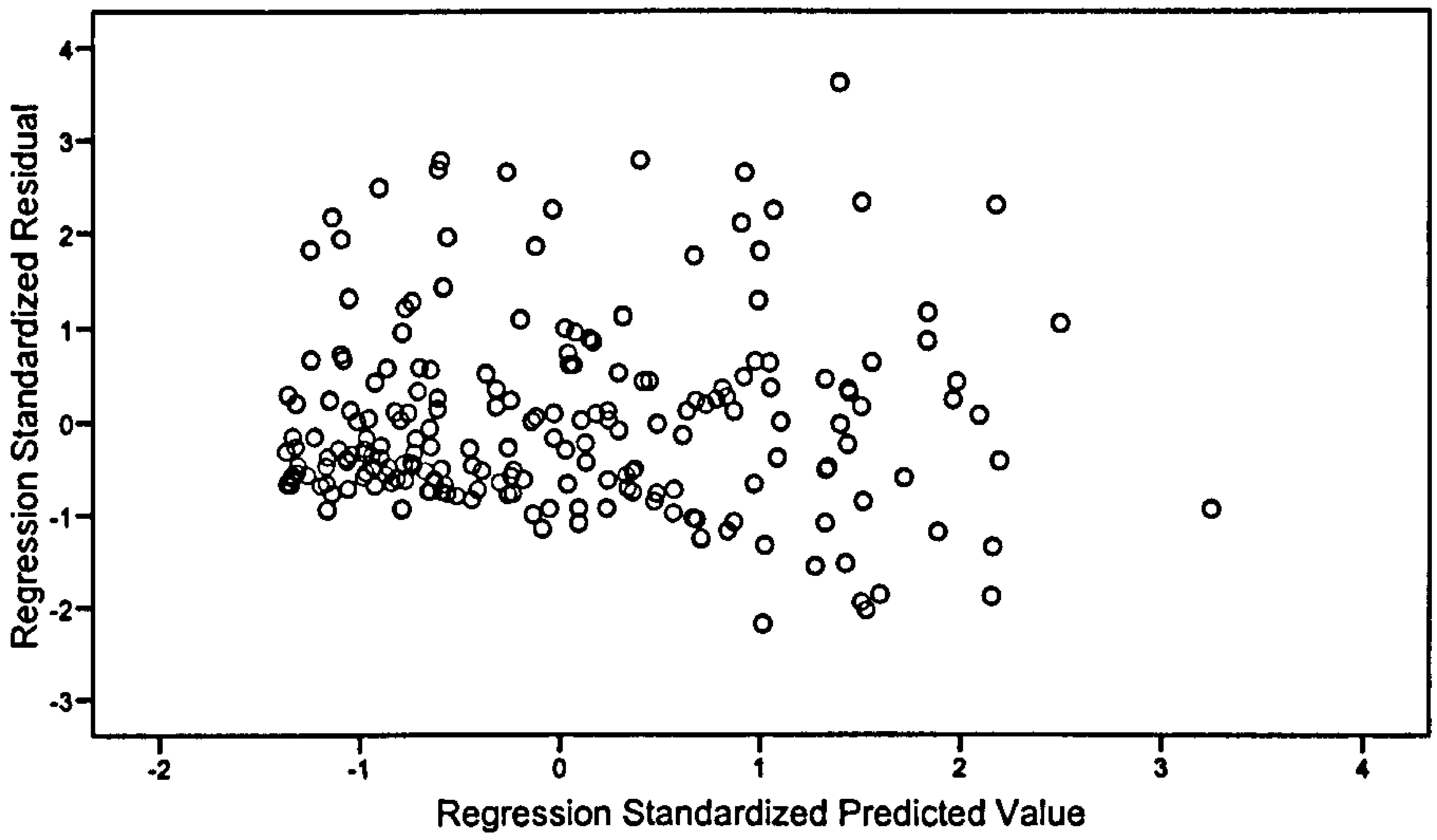


Figure 5.9 A standardised residual plot suggesting homoscedascity within the drained data.

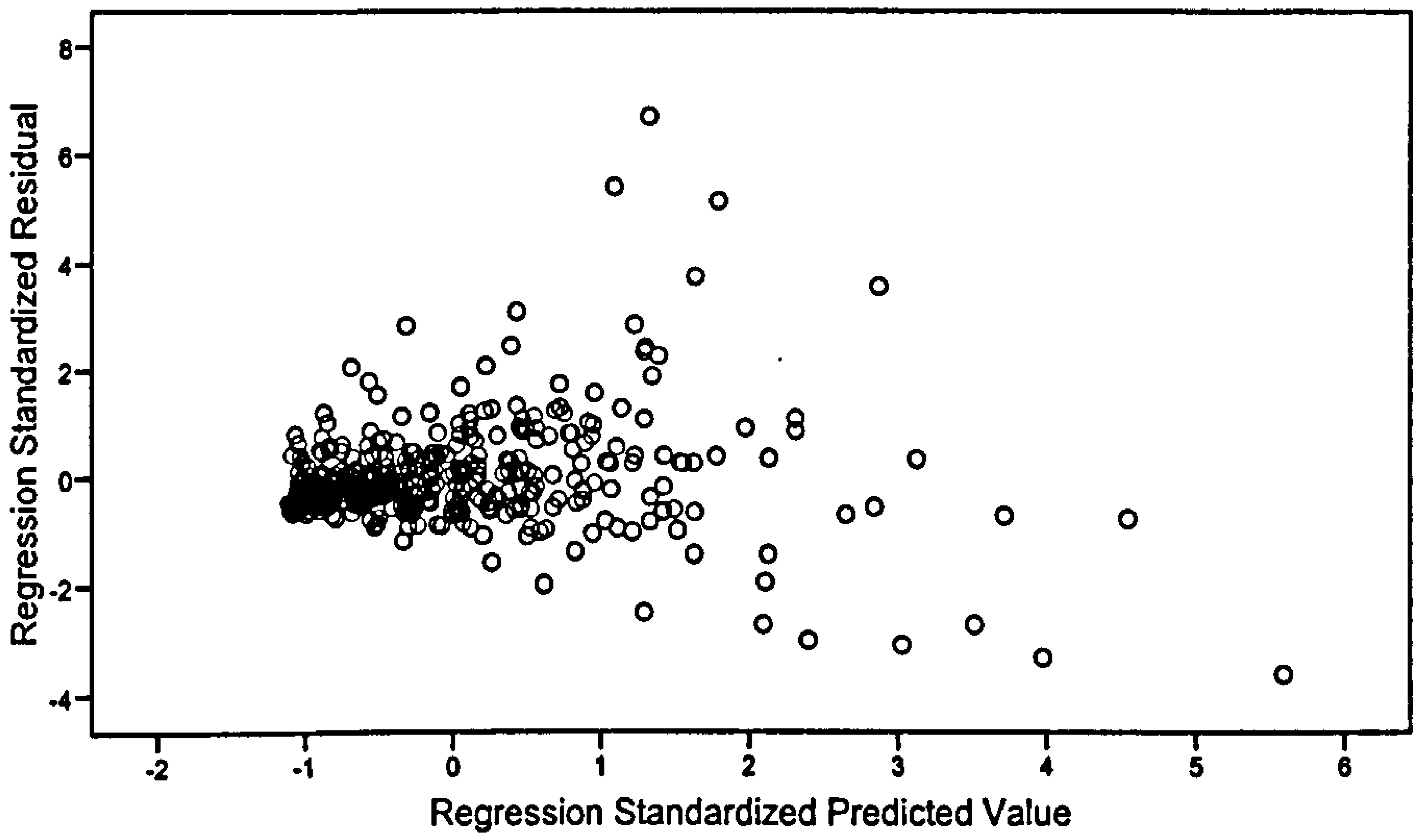
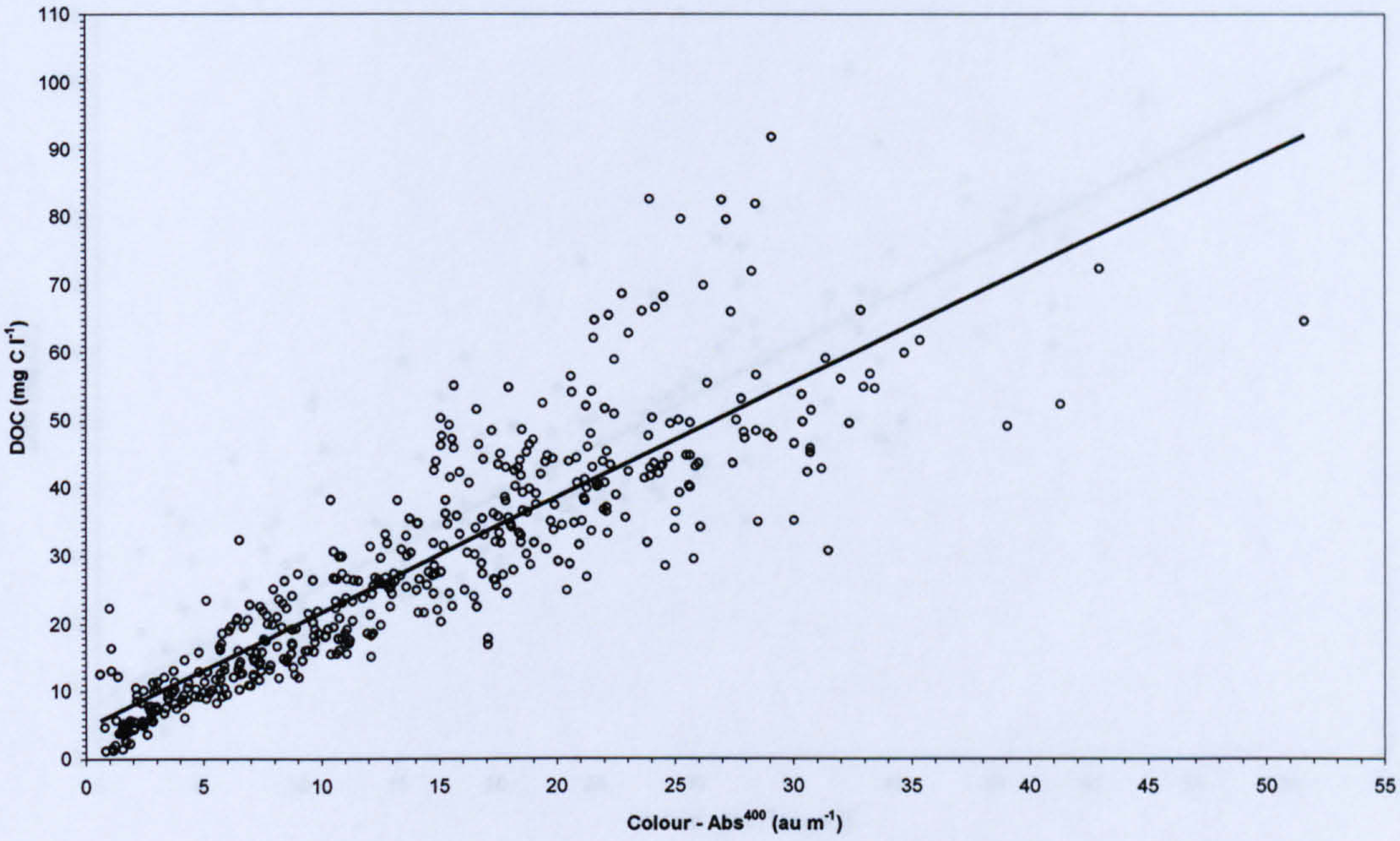


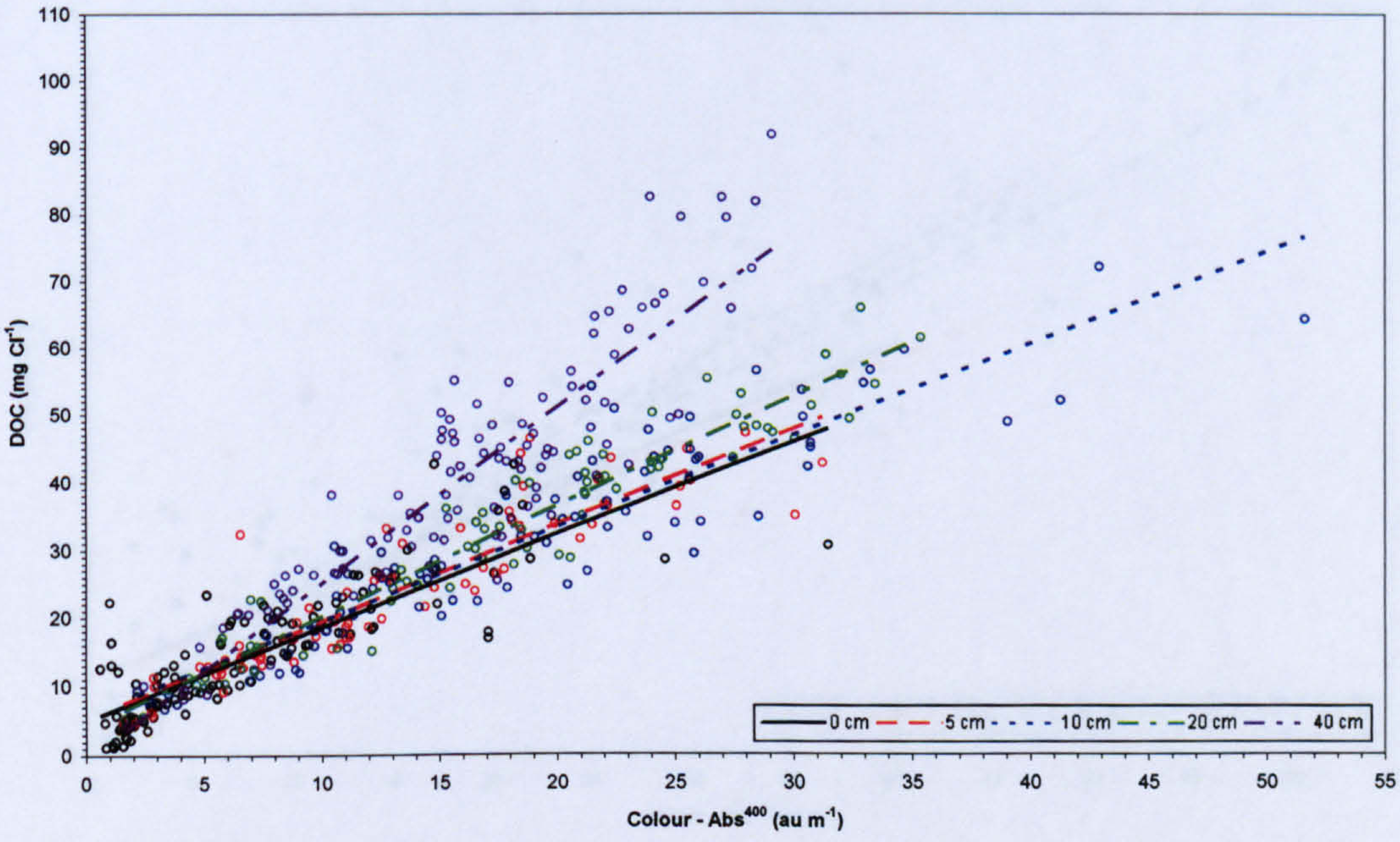
Figure 5.10 A standardised residual plot identifying a tendency towards heteroscedascity within the blocked data.

Table 5.2 further highlights the variability in the colour – carbon relationship, as the individual equations clearly differ between the three sites. However, analysis of the scatter and residual plots presented for each of the three land managements suggests that there may also be variability in the colour – carbon relationship within each of the three sites. For example, in Figure 5.11a although there is a strong relationship between DOC and colour at the intact site, it is apparent that the spread in the data still seems to increase with elevated DOC and colour values. In addition, assessment of the residuals in Figure 5.8 highlights a tendency towards heterogeneous variability. However, when the data for the intact site is broken down into sample depth sub-groups, as seen in Figure 5.11b, clear deviations between the individual depth regressions can be observed, and this divisional method of approach appears to provide a reduced spread of data across the regression lines. Similar results were observed at the drained and blocked sites when the DOC and colour data was broken down in to depth categories, although the apparent difference between the individual regression lines appears to be slightly reduced relative to the intact site (Figures 5.12a – 5.13b). This suggests that the alterations made to DOC production and transportation mechanisms as a result of drainage and restoration may influence the colour – carbon relationship.

When the depth-specific groups were analysed across all three treatments, the biggest difference between regression lines occurred between 5 and 40 cm; thus further comparisons were made between these two depths for each site. As found when performing the site-specific assessment, the depth-specific regressions appear to improve the accuracy of the models (as seen by the reduction in the size of the residuals) with the range in error values falling by between 13 % and 53 % (Table 5.3). For example, at the intact treatment the site-specific data provided a relatively strong correlation of 0.87 and a R^2 of 76 %, and the residuals ranged in size from -27.72 up to 37.88. However, when the data for the intact site was broken down for depth-specific analysis the correlation and R^2 values increased to 0.91 and 83 % respectively at both depths, whilst the range in residual values was reduced by over 50 % at 5 cm depth and by almost 40 % at 40 cm. Furthermore, Figures 5.14 – 5.25 demonstrate that the sub-division of the data by both site and depth categories made significant improvements to the regression models, with the spread of the residuals in

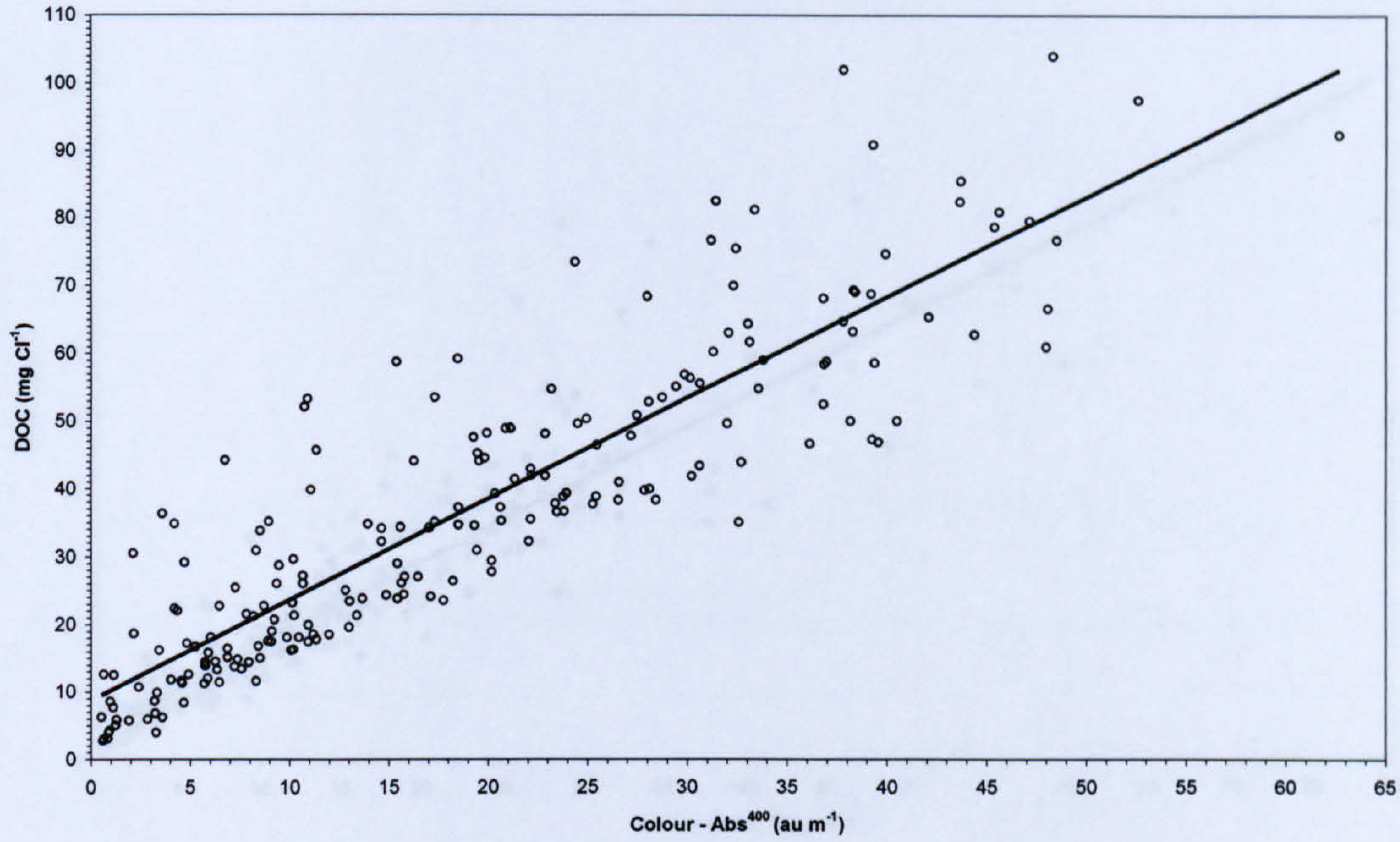


a)

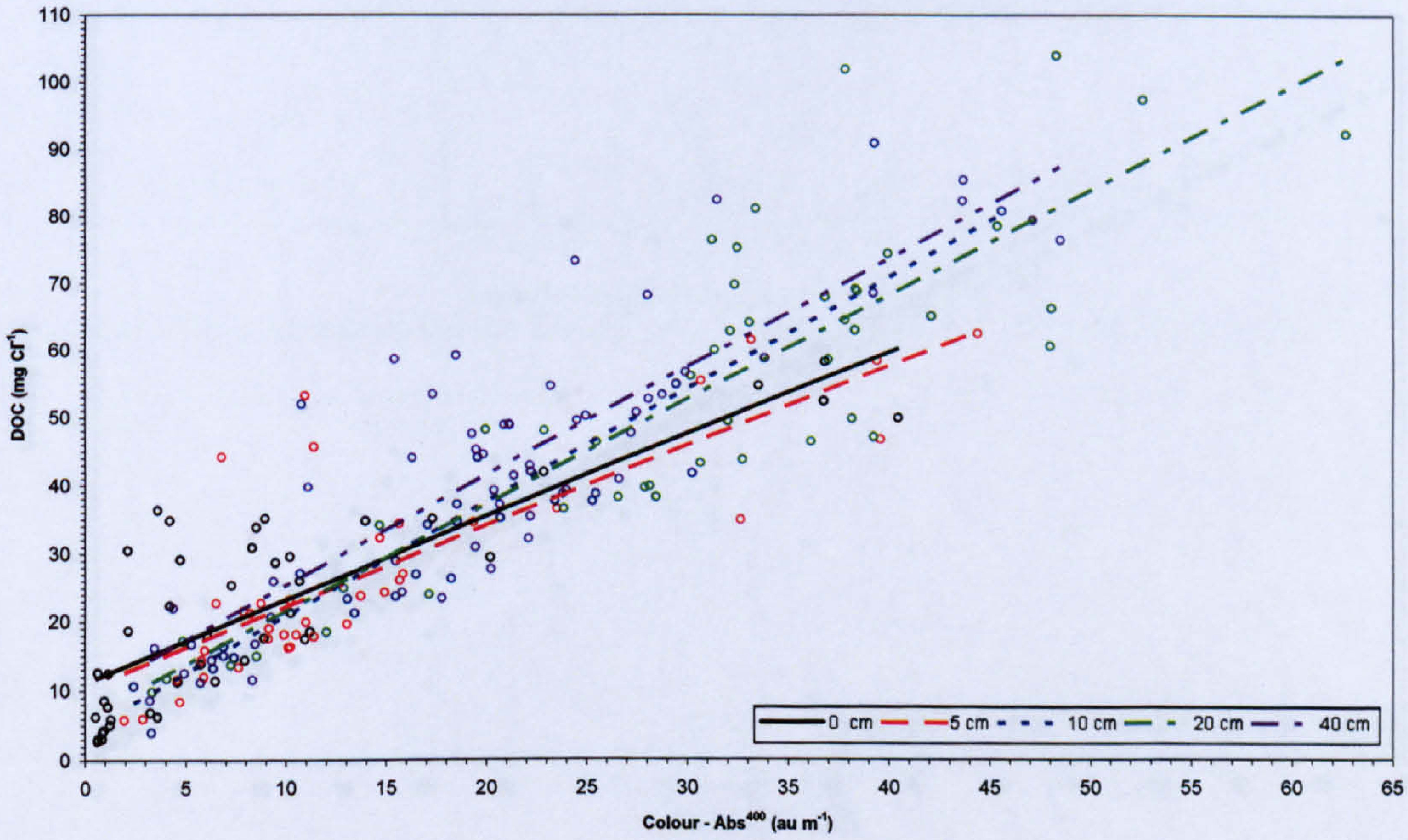


b)

Figure 5.11 The relationship between DOC and colour (Abs^{400}): a) at the intact site; b) by depth at the intact site.

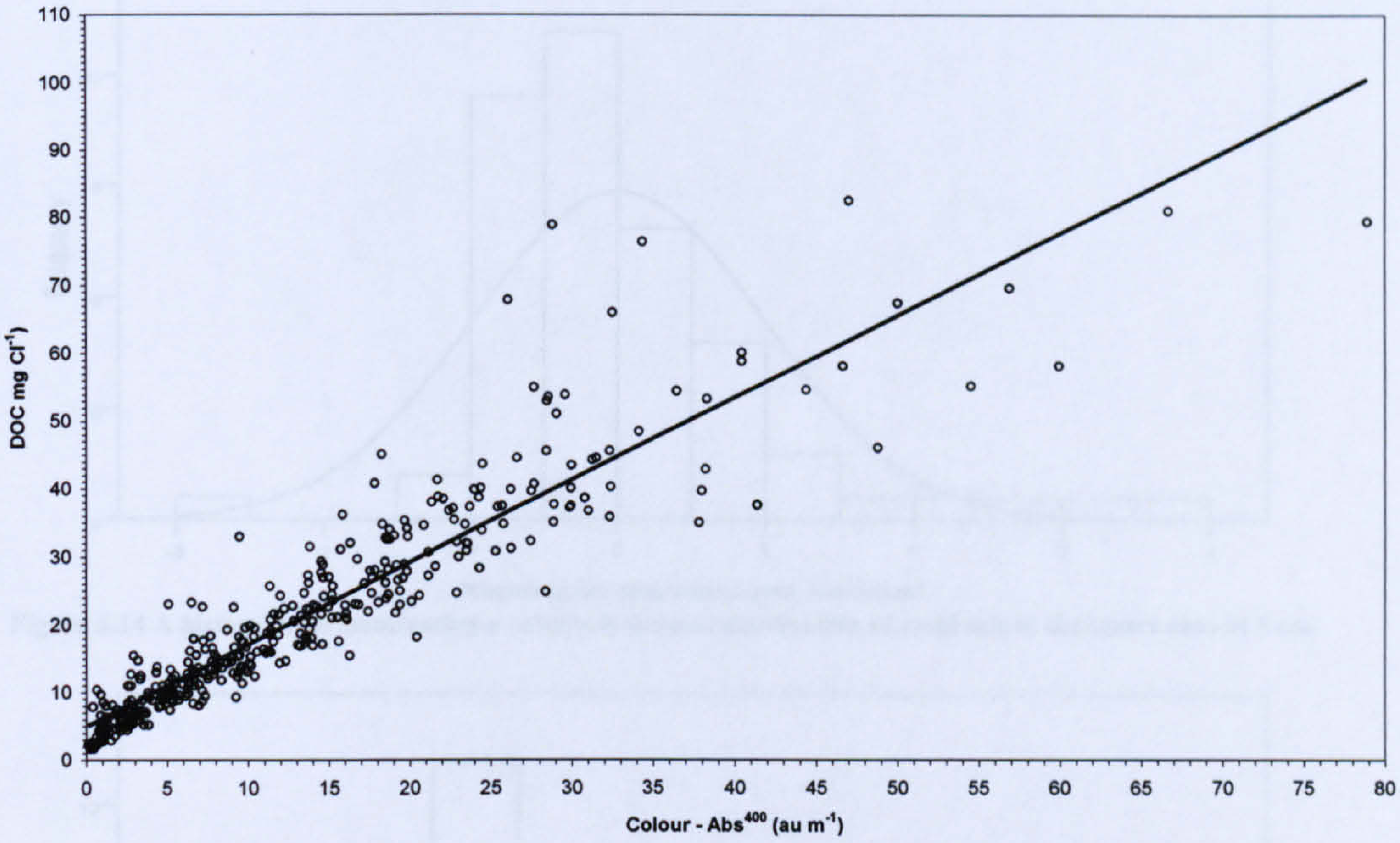


a)

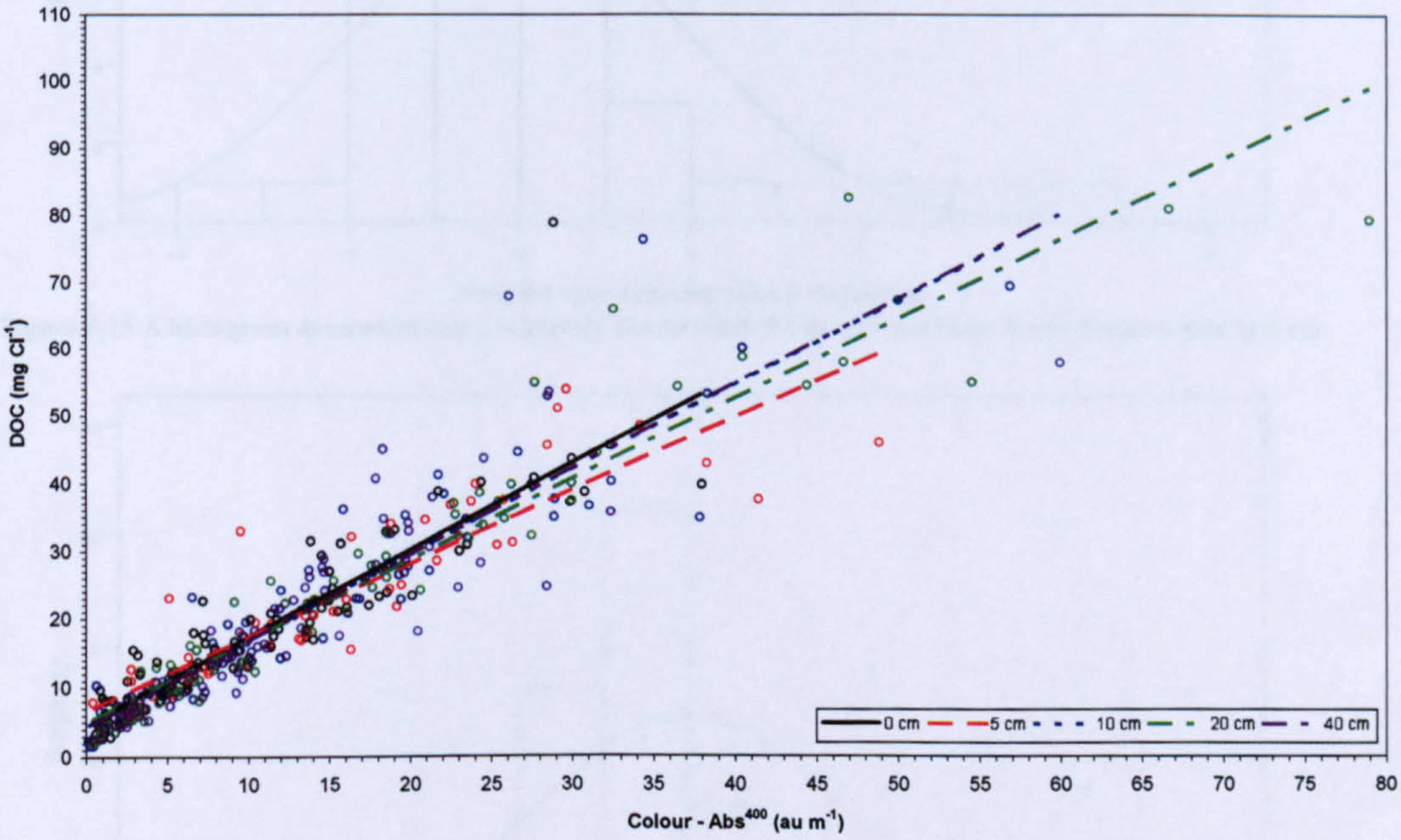


b)

Figure 5.12 The relationship between DOC and colour (Abs^{400}): a) at the drained site; b) by depth at the drained site.



a)



b)

Figure 5.13 The relationship between DOC and colour (Abs^{400}): a) at the blocked site; b) by depth at the blocked site.

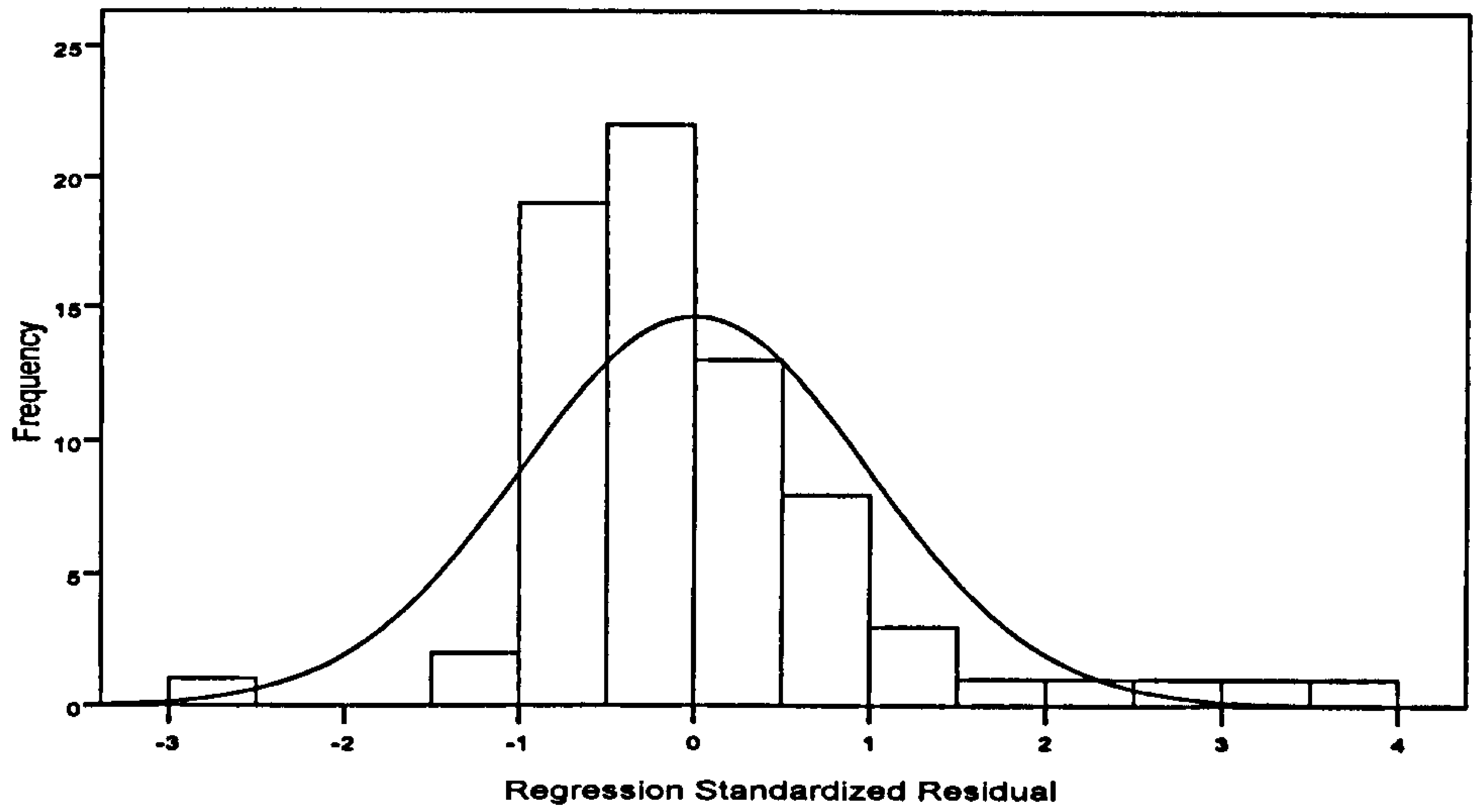


Figure 5.14 A histogram demonstrating a relatively normal distribution of residuals in the intact data at 5 cm.

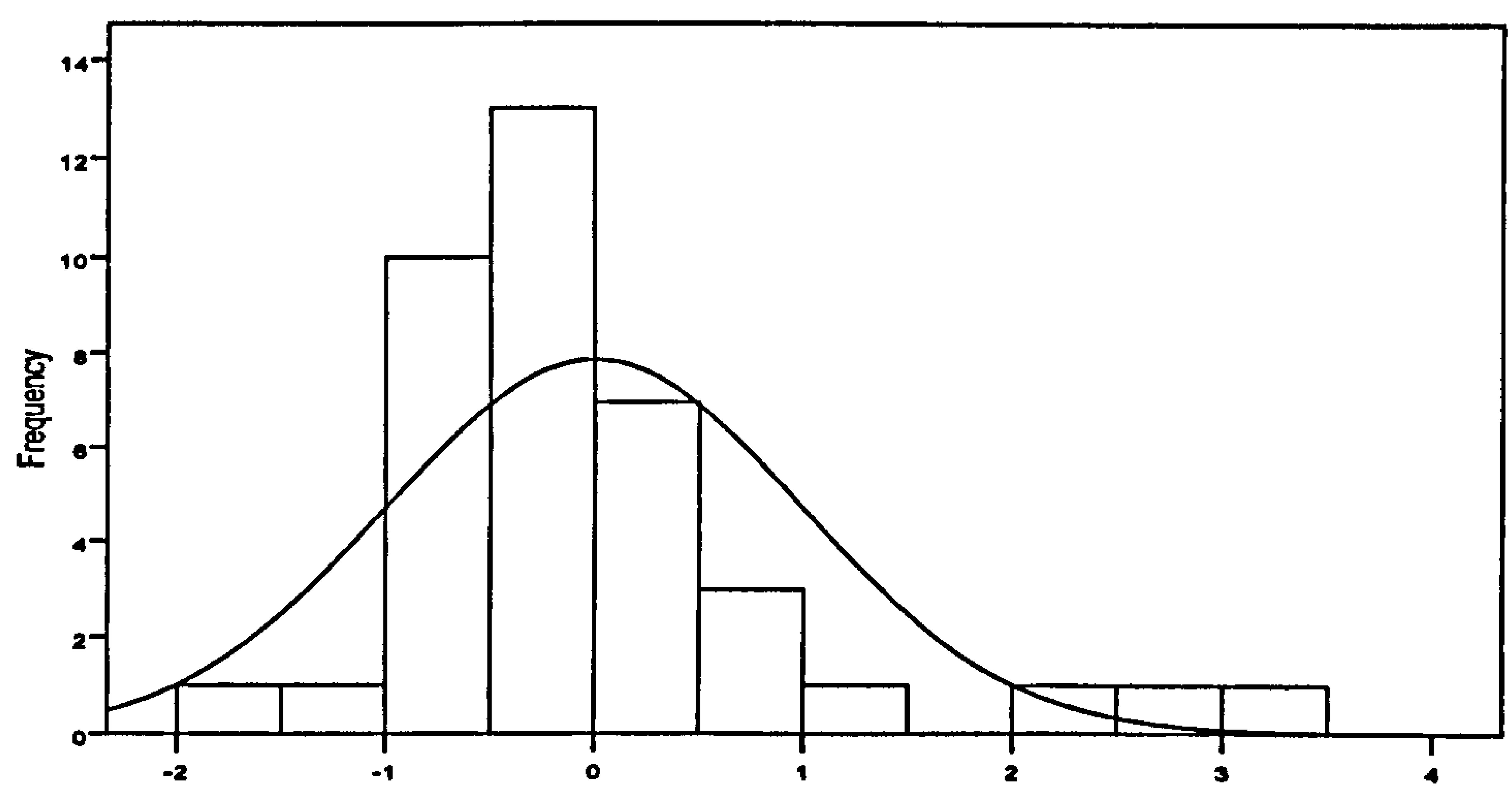


Figure 5.15 A histogram demonstrating a relatively normal distribution of residuals in the drained data at 5 cm.

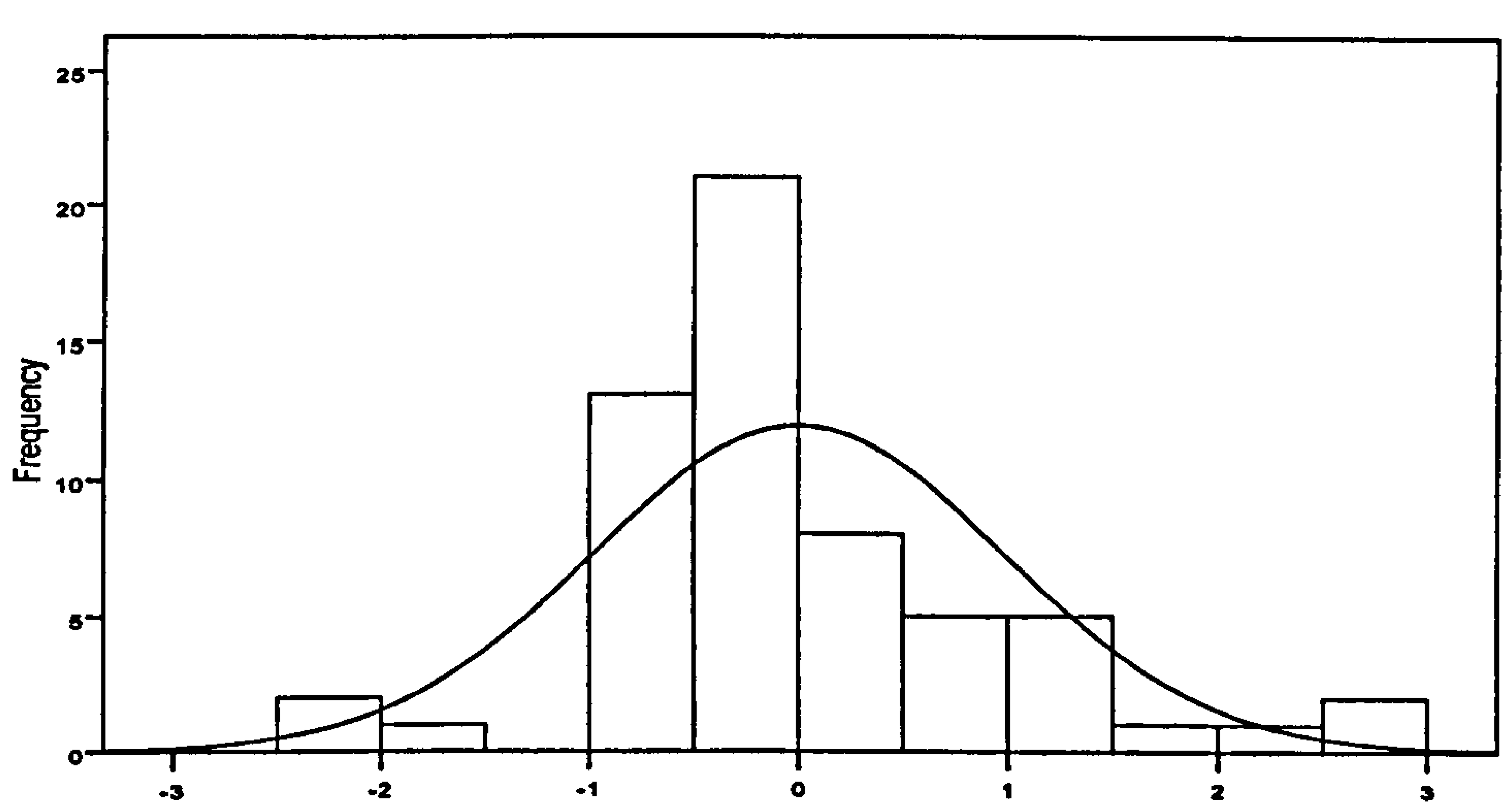


Figure 5.16 A histogram demonstrating a relatively normal distribution of residuals in the blocked data at 5 cm.

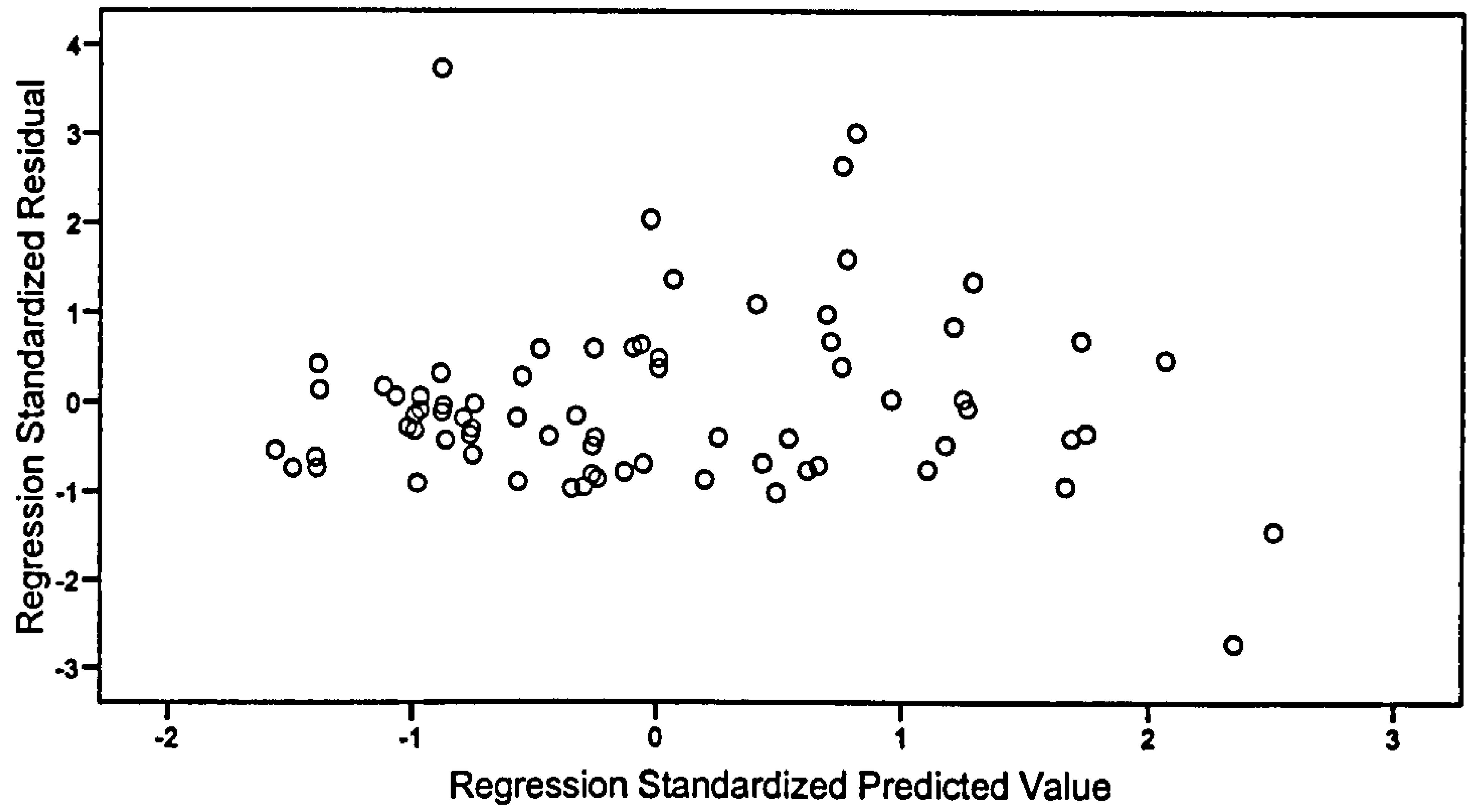


Figure 5.17 A standardised residual plot suggesting homoscedascity within the intact data at 5 cm.

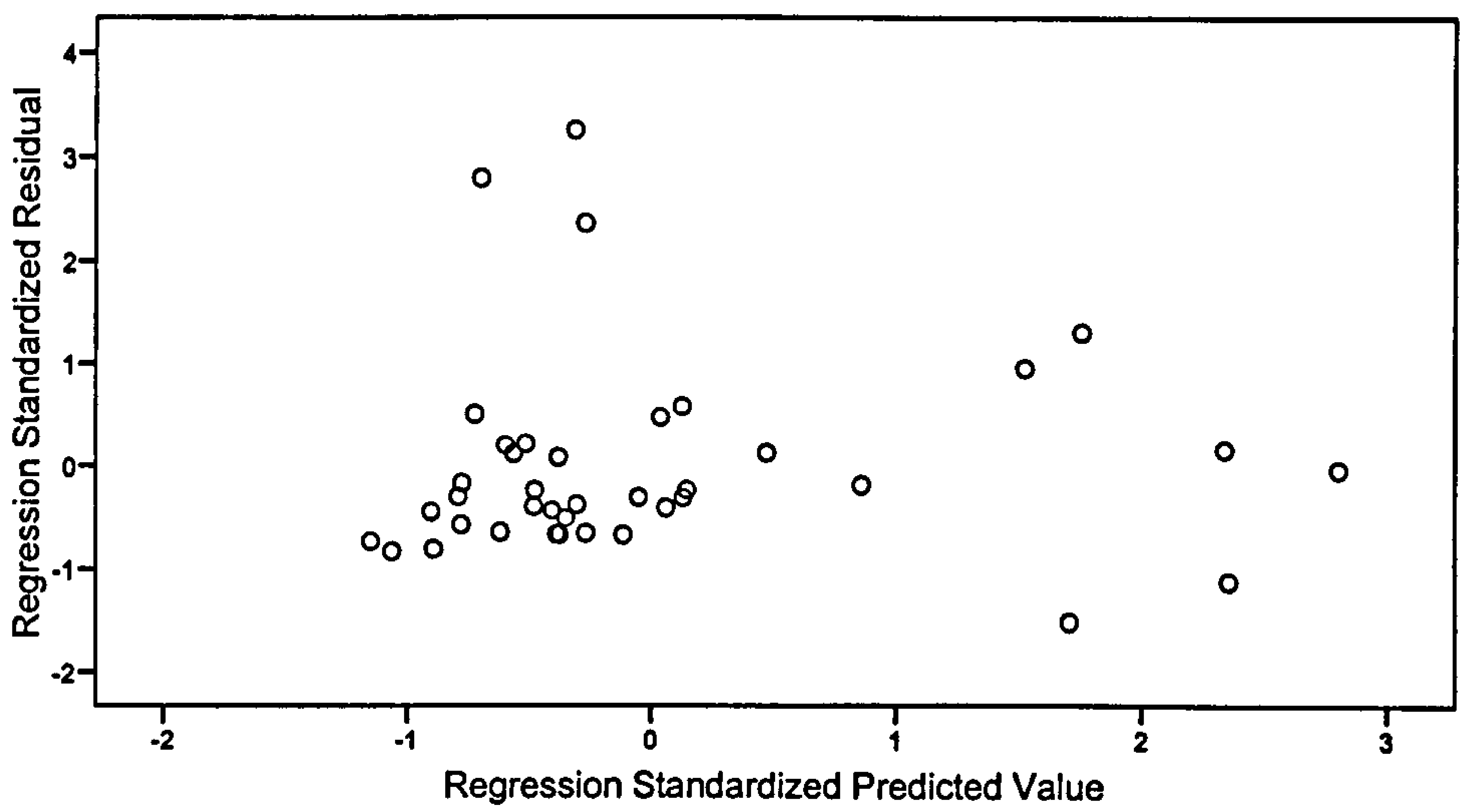


Figure 5.18 A standardised residual plot suggesting homoscedascity within the drained data at 5 cm.

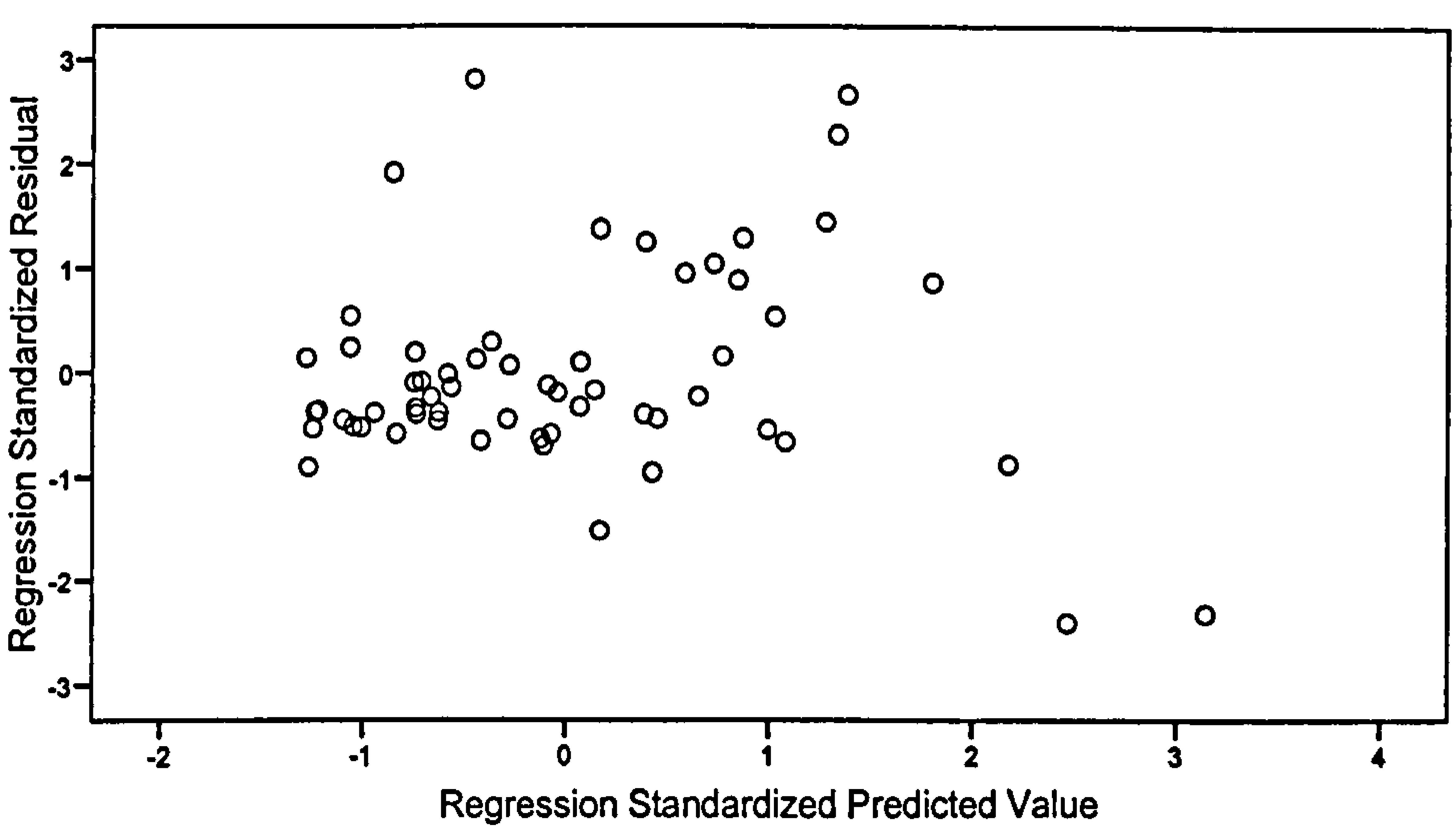


Figure 5.19 A standardised residual plot suggesting homoscedascity within the blocked data at 5 cm.

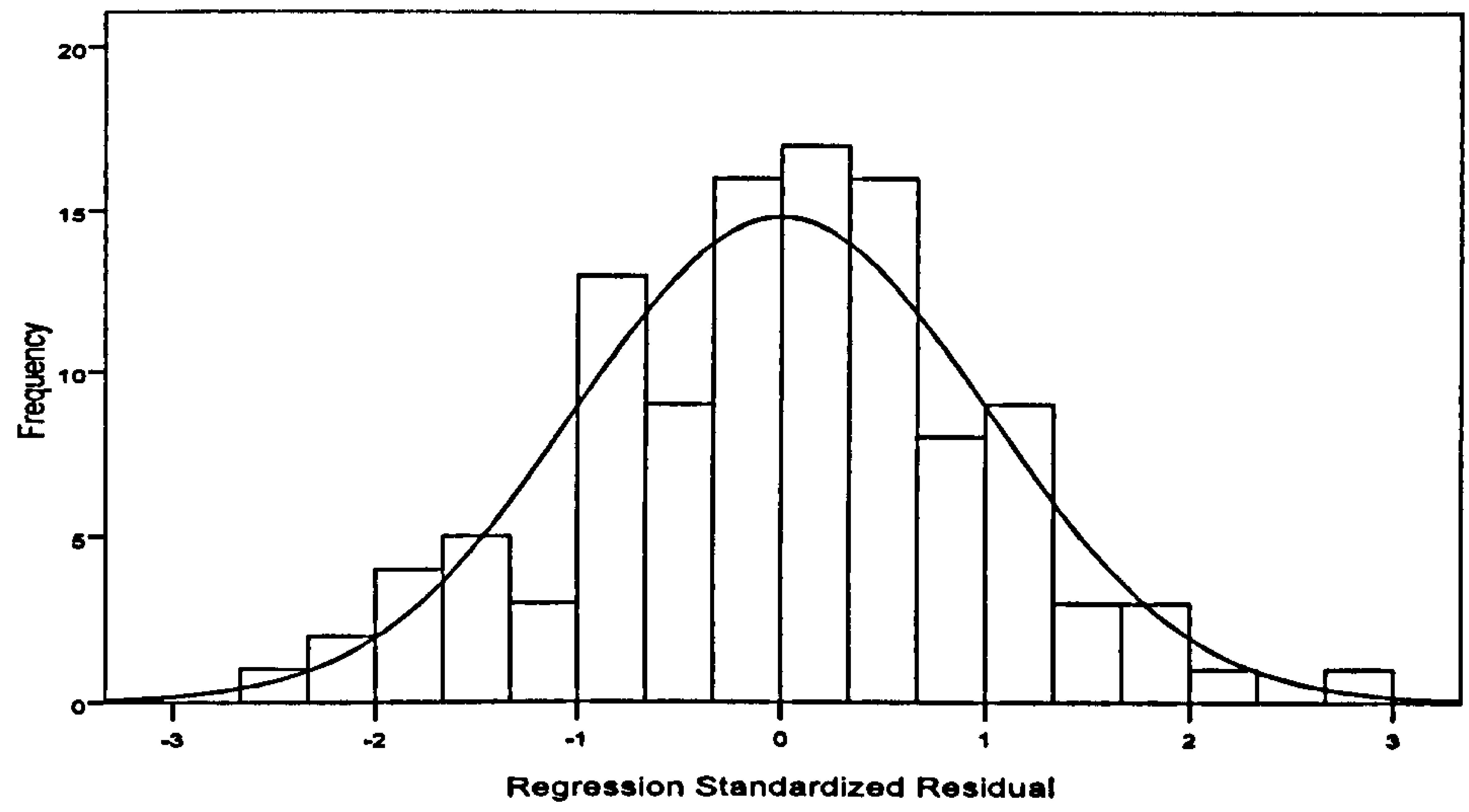


Figure 5.20 A histogram demonstrating a relatively normal distribution of residuals in the intact data at 40 cm.

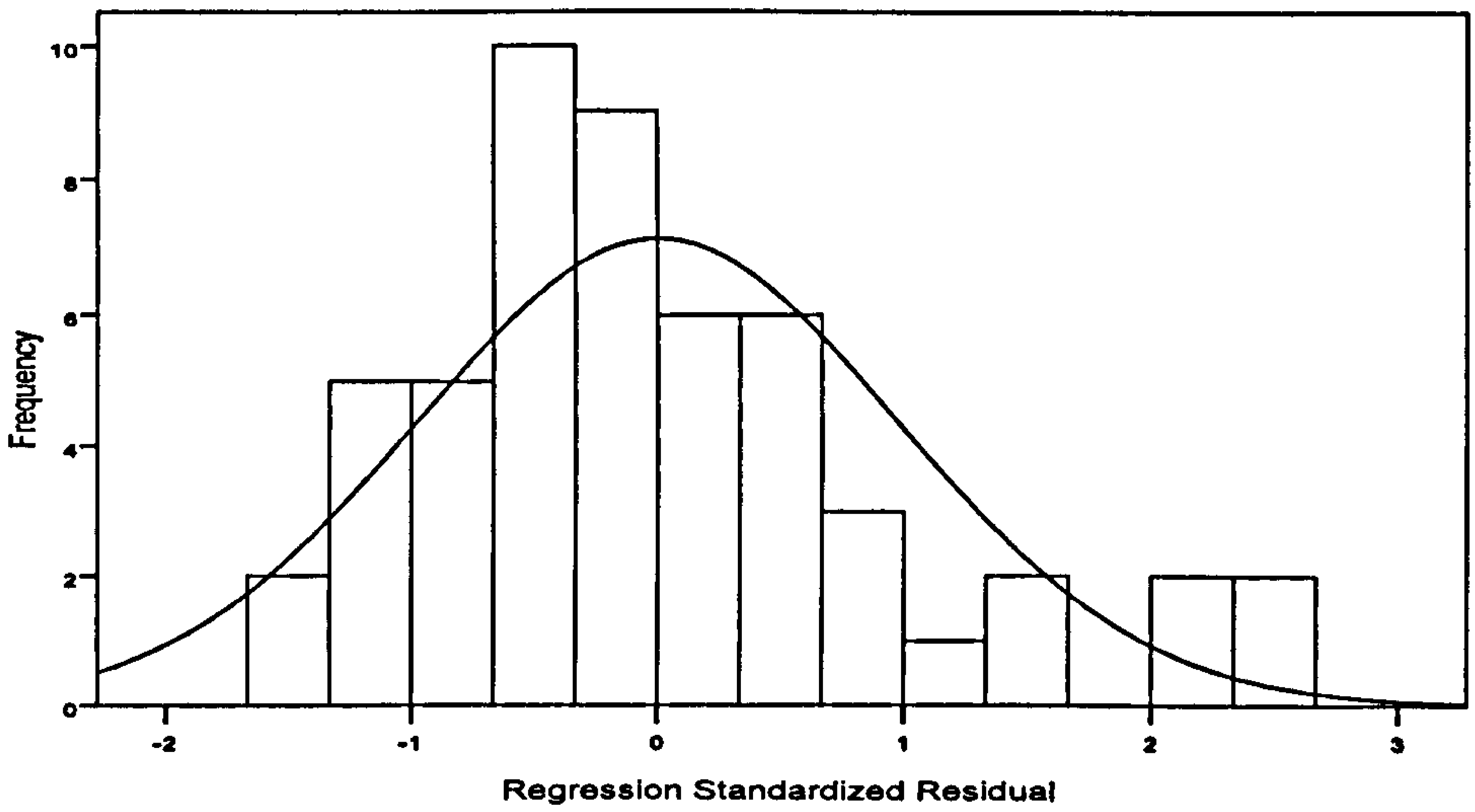


Figure 5.21 A histogram demonstrating a relatively normal distribution of residuals in the drained data at 40 cm.

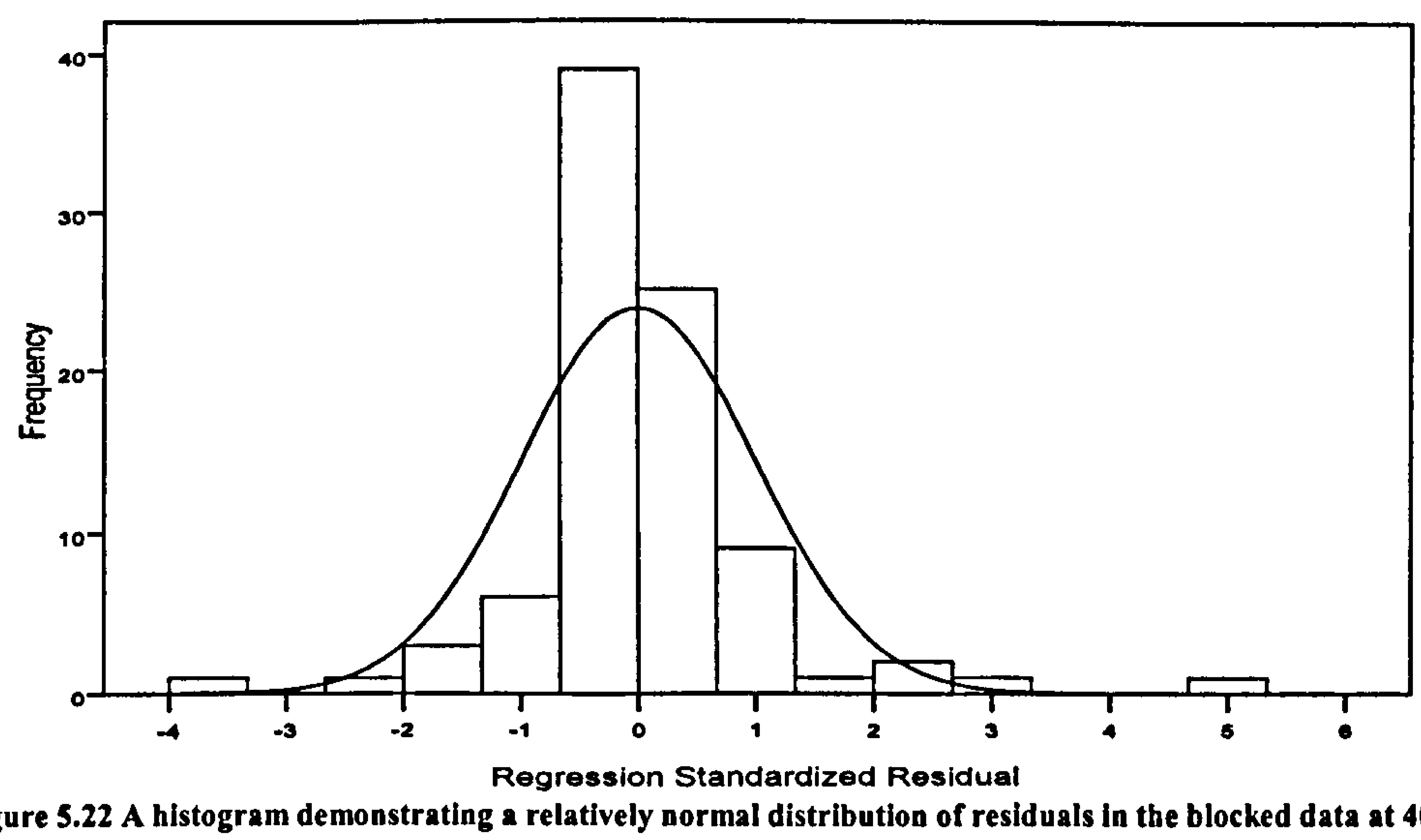


Figure 5.22 A histogram demonstrating a relatively normal distribution of residuals in the blocked data at 40 cm.

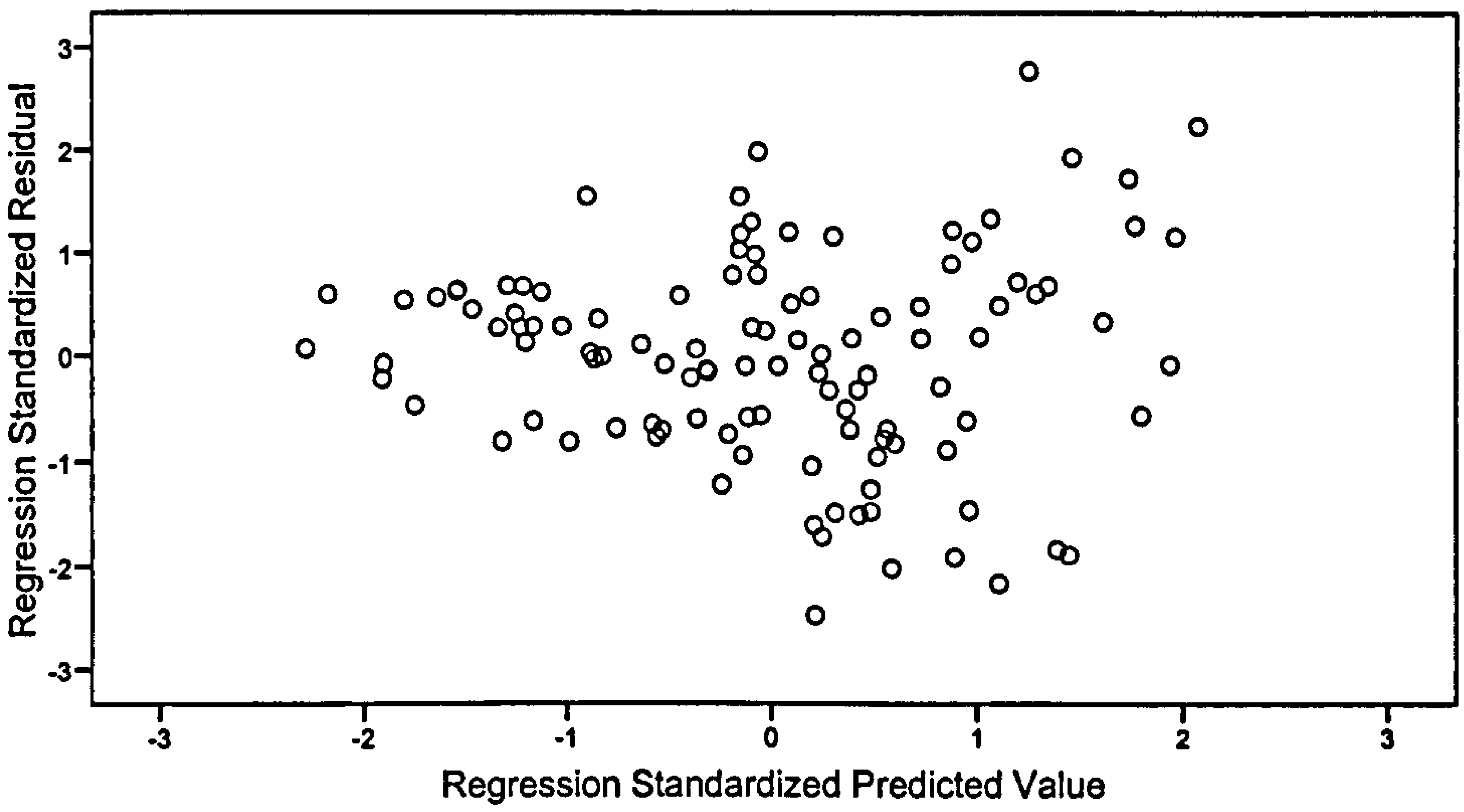


Figure 5.23 A standardised residual plot suggesting homoscedascity within the intact data at 40 cm.

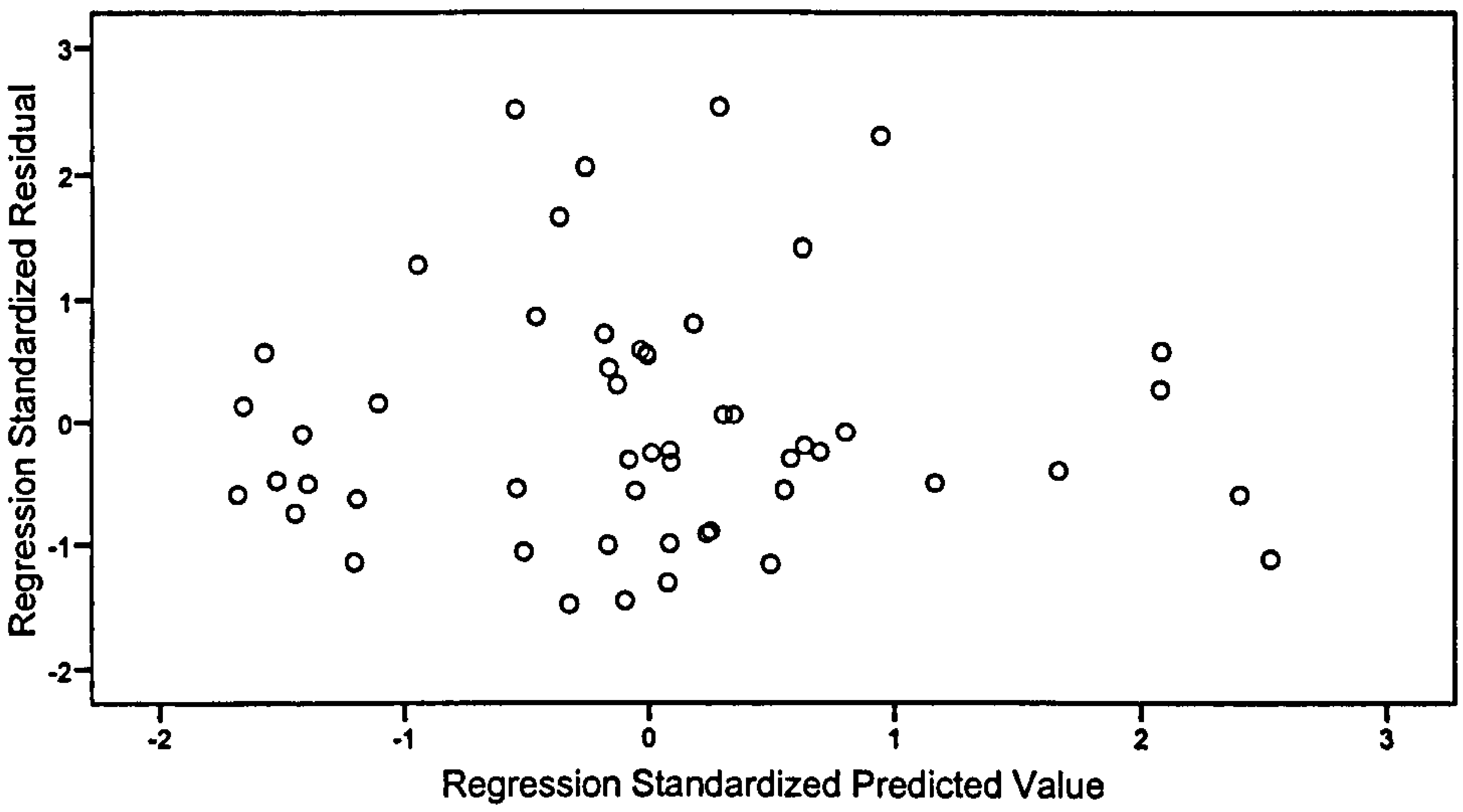


Figure 5.24 A standardised residual plot suggesting homoscedascity within the drained data at 40 cm.

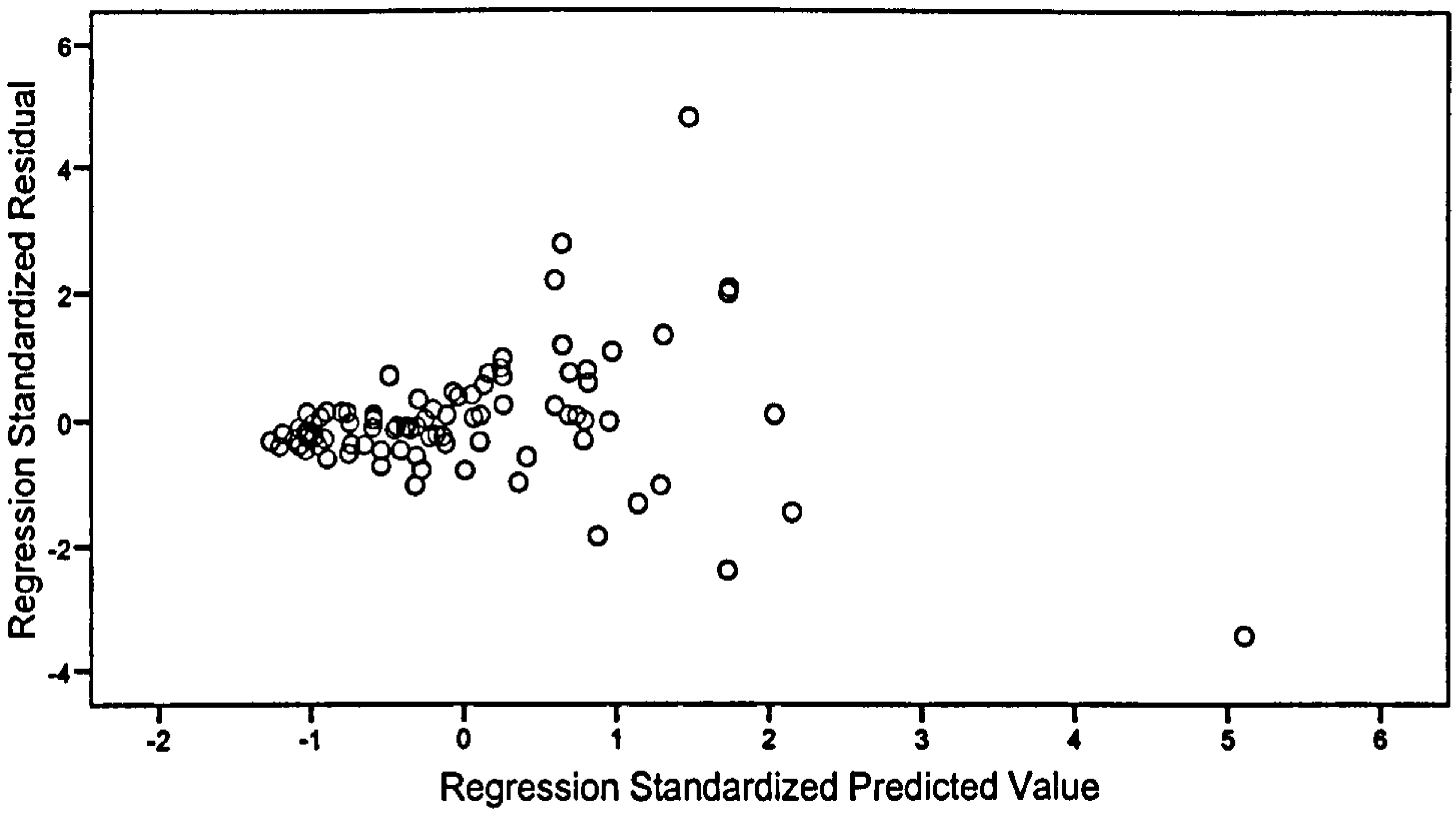


Figure 5.25 A standardised residual plot identifying heteroscedascity within the blocked data at 40 cm.

all but one case (e.g. 40 cm depth for the blocked site) exhibiting a relatively even and random dispersal. This suggests that the assumption of homoscedascity is more closely met, and thus the validity of these depth-specific models is greatly improved.

Following this, ANCOVA was used to test for differences in the regression equations between the depths of 5 cm and 40 cm at each site, and between sites by comparing equivalent soil depths. At the intact site, significant (p <0.001) differences were found in both the slopes and the intercepts of the 5 cm and 40 cm depth equations. In contrast, although deviations in the colour – carbon relationship between depths were observed at the drained and blocked treatments, significant (p <0.001) differences were only found between the slopes at these sites (Table 5.4). When the regression equations were compared between sites using data taken from equivalent soil depths at each, significant (p <0.001) differences were found in the all the slope and intercepts comparisons at 40 cm. At 5 cm however, significant (p <0.001) differences were only found between the slope and intercepts of the intact and blocked sites and the intercept of the drained and blocked sites, whilst differences in slope between the intact and drained sites was significant at p = 0.05. The data was also assessed on a seasonal basis by sub-dividing the paired DOC-Abs^{400} values for each treatment into individual sample date groups. After residual analysis indicated that the temporal data generally met the assumptions of homoscedascity and normality, ANCOVA was performed; this identified that there were significant (p <0.001) differences in both the intercept and slopes of regression lines between sample dates at each site.

The nature of the variability in the colour – carbon relationship is demonstrated by comparing coloured water samples and trying to predict the DOC concentration. For example, at the intact site the mean DOC and Abs^{400} of samples taken from 5 cm depth was 22.29 mg C l^{-1} and 13.47 au m^{-1}, which gives a C/C ratio of 0.60, whilst at 40 cm the mean DOC and Abs^{400} values were 36.83 mg C l^{-1} and 15.37 au m^{-1}, giving a C/C ratio of 0.42. This relatively large difference in the C/C ratio means that on average, a soil water sample at 5 cm contains about 40 % more colour per carbon unit than 40 cm at the intact site. In addition, using the depth-specific equations presented in Table 5.4 it can be seen that for a water sample exhibiting an Abs^{400} value of 20.00 au m^{-1}, the DOC concentration at 5 cm would be 33.72 (± 1 SE = 0.78) mg C l^{-1}, whereas at 40 cm it would be 51.20 (± 1 SE = 0.73) mg C l^{-1}. This variability in the regression equations between depths at the intact site equates to a difference of over 50 % in the predicted DOC concentrations when identical Abs^{400} values are used. Meanwhile, at the drained site the mean DOC and Abs^{400} of samples taken from 5 cm depth were 25.47 mg C l^{-1} and 12.42 au m^{-1} respectively, which results in a C/C ratio of 0.49, whereas at 40 cm the mean DOC and Abs^{400} values were 38.85 mg C l^{-1} and 20.24 au m^{-1}, giving a C/C ratio of 0.52. The deviation in the colour – carbon relationship by depth and between sites means that if an identical Abs^{400} value of 20.00 au m^{-1} is used in the drained depth-specific equations, the predicted DOC concentrations would be 34.07 (± 1 SE = 1.68) and 41.59 (± 1 SE = 1.36) for 5 cm and 40 cm respectively. This means that the DOC concentrations predicted for samples taken from comparable soil depths but from different sites can vary by as much as 23 %.

	Min Residual*	Max Residual*	Correlation#	R^2	n
Intact – Site-specific +	-27.72	37.88	0.87	76 %	457
Intact – Depth-specific ° (5 cm)	-12.91	17.77	0.91	83 %	73
Intact – Depth-specific ° (40 cm)	-19.01	21.27	0.91	83 %	111
Drained – Site-specific +	-22.27	36.99	0.89	80 %	208
Drained – Depth-specific ° (5 cm)	-14.04	30.01	0.81	66 %	39
Drained – Depth-specific ° (40 cm)	-14.47	24.72	0.87	76 %	53
Blocked – Site-specific +	-21.13	38.98	0.93	86 %	382
Blocked – Depth-specific ° (5 cm)	-13.78	16.09	0.90	81 %	59
Blocked – Depth-specific ° (40 cm)	-22.01	30.60	0.88	78 %	89

* = The residual of the error term, i.e. the minimum and maximum differences between predicted DOC and actual DOC.

= Spearman rank correlation, all significant at $p = 0.01$.

+ = DOC values are predicted from Abs^{400} data collected from an individual site using a "site-specific" regression equation that was created from the paired DOC-Abs^{400} samples collected from all the depths sampled at that site.

° = DOC values are predicted for a particular soil depth from Abs^{400} data collected from an individual site using a "depth-specific" regression equation that was created using only the paired DOC-Abs^{400} samples collected from the specific depth under investigation.

Table 5.3 Correlation and regression statistics for site-specific and depth-specific analysis.

The regression intercepts identified in Tables 5.2 & 5.4 are highly variable. Low intercept values indicate that most of the DOC present is in a form that absorbs at 400 nm and is therefore coloured, whilst high intercepts indicate a greater portion of the DOC does not absorb at 400 nm and is therefore un-coloured. As an example, if the intercept for 5 cm depth at the drained site (10.32 mg C l^{-1}) is taken as a proportion of the mean DOC concentration for this depth (25.47 mg C l^{-1}), it suggests that as much as 40 % of the DOC is comprised of un-coloured organic material and is thus undetectable using spectrophotometric analysis. Therefore, the intercept also provides the minimum value for which DOC can be predicted, and indicates that the use of colour can incur a low level of precision.

	Colour – Carbon Regression Equation (± 1 SE)	n
Intact – Site-specific	$DOC = 1.70 (\pm 0.05) \times Abs^{400} + 4.68 (\pm 0.75)$	457
Intact – Depth-specific (5 cm)	$DOC = 1.42 (\pm 0.08) \times Abs^{400} + 5.25 (\pm 1.14)$	73
Intact – Depth-specific (40 cm)	$DOC = 2.60 (\pm 0.12) \times Abs^{400} - 0.77 (\pm 2.02)$	111
Drained – Site-specific	$DOC = 1.49 (\pm 0.05) \times Abs^{400} + 8.74 (\pm 1.22)$	208
Drained – Depth-specific (5 cm)	$DOC = 1.19 (\pm 0.14) \times Abs^{400} + 10.32 (\pm 2.49)$	39
Drained – Depth-specific (40 cm)	$DOC = 1.61 (\pm 0.13) \times Abs^{400} + 9.33 (\pm 3.01)$	53
Blocked – Site-specific	$DOC = 1.21 (\pm 0.03) \times Abs^{400} + 4.96 (\pm 0.45)$	382
Blocked - Depth-specific (5 cm)	$DOC = 1.08 (\pm 0.07) \times Abs^{400} + 6.61 (\pm 1.24)$	59
Blocked - Depth-specific (40 cm)	$DOC = 1.27 (\pm 0.07) \times Abs^{400} + 4.22 (\pm 1.12)$	89

Table 5.4 Site-specific and depth-specific regression equations.

5.4. DISCUSSION

A strong correlation was found between colour and DOC in the pooled dataset of soil water samples, with regression analysis showing there to be a relatively high coefficient of determination, which indicates that most of the variance in the samples can be explained by the model. However, it seemed that the assumption of homoscedascity had been violated as the spread of the data appeared to increase as DOC and colour values increased and a fan-shape was observed in the residual analysis. Consequently, the data was divided into sample sub-groups with respect to land management, soil depth and sampling month, which in most cases was found to increase the strength of the correlation and the coefficient of determination, and reduce the size of the largest residuals, in some cases by as much 54 %.

To test whether there was any significant variation in the colour – carbon relationship between the sub-groups, the intercepts and slopes of the individual regression lines were compared. Significant differences were found between sites, soil depths and sample months, indicating that the nature of the relationship varies between peat layers, land managements, and through time, with the DOC concentration of samples exhibiting identical Abs^{400} values found to vary by over 50 %. Thus, the proportion of coloured organic matter in soil water DOC is clearly highly variable, and the spectrophotometric determination of DOC concentrations in these environments using pooled DOC-Abs^{400} data incurs a low degree of accuracy.

Such findings are likely to have a direct impact on fluvial carbon budget research given the number of studies reliant upon using a single regression equation to monitor and predict DOC export from water colour measurement alone (e.g. Dobbs *et al.* 1972; Mattson *et al.* 1974; Moore & Jackson 1989; Moore 1987; Tao 1998; 2005; 2004; Worrall *et al.* 2002; 2003; 2004). For example, Moore (1987) and Moore and Jackson (1989) used spectrophotometric analysis to monitor the changes in the concentration of DOC released from drained and harvested bogs located in southern Quebec and Westland, New Zealand. Furthermore, Worrall *et al.* (2002) used a single calibration between DOC and water colour to predict the DOC release from an upland blanket peat catchment during an autumn flush event, which was followed by Worrall *et al.* (2003) who used the same equation to predict DOC concentrations over a 38-year period for two additional catchments where DOC had never been recorded.

It was also identified that when compared to the direct determination of DOC using combustion-infrared methods, which have a stable minimum detection limit of 1.0 mg C l^{-1}, spectrophotometric analysis exhibited a highly variable detection limit of up to 10.32 mg C l^{-1}. Not only does this identify that the use of colour as a proxy for the true determination of DOC entails a low level of precision and is thus inappropriate for measuring low DOC concentrations, but it also suggests that as much as 40 % of DOC can be comprised of uncoloured organic matter. This corroborates the findings of Thurman (1985) who found that although coloured humic substances are generally the dominant fraction in DOC, their contribution varies by between 30 and 90 %, and Qualls and Richardson (2003) who identified that DOC released from the Everglades was composed of about 50 % coloured humic substances. In addition, Zsolnay and Steindl (1991) identified that although the (coloured) refractory portion of DOC remains relatively constant, the (uncoloured) labile fraction ranges between 16 and 68 %. This suggests that in some cases up to 70 % of DOC can be composed of small, uncoloured non-humic compounds such as carbohydrates, proteins, amino-acids and fats. Thus, as the ratio of the differently coloured organic compounds that constitute DOC varies, the samples will absorb different quantities of light and therefore provide different responses in spectrophotometric analysis regardless of whether the overall DOC concentration has changed.

The significant differences identified in the spectrophotometric properties of DOC between peat layers, land managements, and through time, are extremely important because the dominance of water flowpaths in peatlands varies depending on antecedent conditions and topographic position, and most environmental change scenarios envisage considerable modifications to the hydrological routing of water through and across the peat (Freeman *et al.* 2001a; Holden 2005; Holden & Burt 2003c). Therefore, it is highly likely that a soil water sample with a similar colour today compared to that from the same location many years ago may actually have a very different DOC concentration. Consequently, those fluvial carbon studies that have used paired DOC-colour samples collected from one location over a short period in order to reconstruct a DOC record back or forward in time, or that have applied the same equation to additional catchments where DOC was never recorded, should be treated with caution.

In order to produce reliable predictions of carbon losses from peatlands following environmental change, particularly for those studies incorporating spectrophotometric analysis, requires a much greater understanding and integration of the processes likely to control DOC production and transportation, and therefore its composition. It is thought that enhanced levels of decomposition, such as those likely in drained peat, leads to the formation of highly coloured, decay resistant humic organic material, which may inadvertently result in the rate of future carbon loss being less affected by changes in environmental conditions. For example, Hogg *et al.* (1992) found that peat that has already been exposed to long periods of aerobic decay may be highly resistant to further decay, as when a given mass of peat is aerated it may be assumed that most of the organic carbon that is lost from the site will be the more labile non-humic and un-coloured fractions in contrast to the larger more recalcitrant coloured humic fraction. This is likely to be because the humic fraction is more resistant, and perhaps therefore inhibitory, to microbial degradation and thus if coloured humic fractions are allowed to build up, they could prevent further degradation (Alkan *et al.* 2007; Cannell *et al.* 1993; Qualls & Richardson 2003).

Thus, it appears that the modified colour – carbon relationship observed at the drained site may have occurred in response to an enhanced level of DOC production in conjunction with the release of a greater amount of DOC sourced from older, more humified material from the deeper soil layers exposed by the lowered water table relative to the intact site. In contrast, it would seem the altered colour – carbon relationship at the blocked site may be the result of a reduction in DOC production and the continued utilization and mineralisation of existing DOC, which has resulted in a further compositional transformation, such that the DOC is even more depleted in non-humic and hydrophilic compounds relative to the drained and intact sites.

This corroborates the findings of Boyer and Groffman (1996) who observed the composition of DOC varied with soil depth and changes in land use when they compared forested and agricultural sites in the Hudson River Valley, USA. They found enhanced DOC concentrations in the agricultural soils were largely caused by an increase in the humic acid fraction, and suggested this was due to functional changes in litter quality and organic matter dynamics. Furthermore, Kalbitz *et al.* (1999) used DOM properties to differentiate between degraded and intact peatlands caused by varying intensities of land use. They found that degraded peat had a higher level of absorbance over a broad wavelength range and a higher SUVA (at 285nm) compared to relatively intact peat, and suggested this was due to an increased amount of humification in the degraded peat, with Zech *et al.* (1997) suggesting that the main transformations were the loss of polysaccharides and phenolic groups, the modification of lignin structures, and the enrichment in recalcitrant, non-lignin aromatic structures.

In addition, Fleck *et al.* (2004) found that peat that had been drained for agricultural production in the Sacremento-San Joaquin Delta California had become heavily oxidised in the top soils layers, and found that wetland restoration changed many of the biogeochemical processes controlling DOC release from peat soils, relative to their previous use as agricultural land. They indicated that organic matter source, extent of soil organic matter decomposition, and decomposition pathways are all factors in the type of DOC released. In addition, Chow *et al.* (2006) found that both the SUVA and hydrophobic acid content were significantly enhanced during wet-dry cycles and wet conditions in the agriculturally drained peat soil of the Sacramento-San Joaquin Delta. They also suggested that this was indicative of an increase in the relative proportion of aromatic carbon in the DOC fraction.

The bioavailability of DOC depends on its chemical composition and is therefore a function of plant type, growth conditions and age, with DOC becoming more recalcitrant with age as physical processes and microbial activity convert available DOC to more refractory compounds through complexation reactions (Boyer & Groffman 1996). For example, Lundquist *et al.* (1999) also observed differences in DOC composition between different land managements in Californian agricultural soils, and found that although DOC concentration, microbial biomass and respiration were significantly higher in an organic field soil compared to a conventional agricultural soil, the proportion of labile DOC was much lower in the organic soil. They suggested that this may be because i) the organic soil microbial community depleted labile DOC to a greater degree than the conventional community; or ii) the type of organic inputs to the soil may have influenced the lability of DOC.

It is apparent that similar processes may also operate on a seasonal basis, as the colour – carbon relationship was found to vary with time, which corresponds well with the findings of Scott *et al.* (1998) who measured the ratio of hydrophilic DOC to total DOC and found that there was a seasonal trend, with the highest values observed during the summer months. However, they found that following a two-month drought in 1995, the ratio of hydrophilic DOC to total DOC fell by 50% and remained lower for the rest of the sampling period. Scott *et al.* (1998) suggested that the increased proportion of hydrophilic DOC during the summer was due to the relative ease of dissolution within the soil of the more hydrophilic fractions and that the concentration of hydrophilic organic compounds in the soil water is strongly related to the activity of the bacteria that produce them. In contrast, they suggested the more hydrophobic compounds are retained by adsorption and/or aggregation processes, and are leached more slowly (Scott *et al.* 1998). In addition, Mladenov *et al.* (2005) studied temporal and spatial variance in the SUVA of DOM to identify its sources and fate during flood events. They found that microbial degradation has an important effect on DOC quality along spatial gradients, with microbial processing of DOM causing recalcitrant DOM to remain in solution, while more labile fractions are consumed. They found several lines of evidence suggesting that the consumption of DOC by bacterial communities may be significant and that the shift in DOC sources, as shown by changes in SUVA measurements, showed that microbial degradation contributes to the removal of DOC with time.

Thus, it seems different levels of oxidation typical of drained and restored blanket peat alters the primary soil organic matter decomposition pathway from anaerobic to aerobic, and it is this change in soil redox conditions that leads to a shift in the micro-organism population responsible for organic matter decomposition and the type of DOC released (Fleck *et al.* 2004). In theory, DOC composition should be controlled by these biotic processes, with temperature dependent seasonal fluctuations and increased concentrations caused by an enhanced mineralisation after changes in environmental conditions (Kalbitz *et al.* 2000). However, variations in water fluxes through soil layers can be equally as important. For example, Izbicki *et al.* (2004) characterised DOC in storm flow from the Santa Ana River in Southern California during 1999-2002 and found that the composition changed rapidly during storm events, and that the fractions of hydrophobic and hydrophilic acids varied depending on where runoff was sourced. Izbicki *et al.* (2004) assessed SUVA and found that DOC that had accumulated in previous dry seasons and that had not been washed off had apparently changed in composition and become more aromatic. They suggested that this was a result of decomposition of simpler, straight-chain, aliphatic carbon compounds such as sugars, starches and waxes. In addition, Jardine *et al.* (1990b) assessed the subsurface transport of DOC through a forested Ultisol soil and found that the hydrophilic component can be preferentially channelled through the soil relative to hydrophobic DOC, which is more strongly adsorbed by the soil.

In contrast, Curtis and Schindler (1997) compared the dependencies of colour and DOC on the hydrologic flushing rate and found that the coloured, light-absorbing components of DOC were removed or transformed from water at rates faster than bulk DOC. They found that colour, measured by absorbance at 350nm appeared to be lost from lake water faster than DOC because the SUVA of organic matter decreased with increasing water residence time, and suggested that this was due either to the photo-bleaching of organic matter or the dilution of DOC by differently sourced DOC that was less-coloured. However, Qualls and Richardson (2003) assessed the factors controlling the concentration, export and decomposition of DOC from the drained peat soils of the Everglades of Florida and found that exposure to solar radiation increased the decay rate of DOC by 25 %. They suggested that this was because after exposure a portion of the humic fraction was converted to hydrophilic acid, which rendered the remaining DOC more susceptible to microbial decomposition. Thus, as UV light can destroy the humic substances, it may also increase the biodegradability of the remaining DOC by removing the inhibitory effects in addition to generating some smaller molecules from the hydrophilic acid fraction which are more accessible to bacterial enzymes.

5.5. CONCLUSION

The colour – carbon relationship in upland blanket peat soil-waters was found to vary significantly between peat layers, land managements, and through time. This is thought to be a result of modifications to processes such as microbial decomposition and mineralisation pathways; hydrological transport/routing; carbon sources and availability; and photodegradation rates, which all have profound effects on the carbon forms available. Subsequently, the use of spectrophotometric analysis as an indirect method of determining DOC concentrations has been brought into dispute, for although there is a significant correlation between water colour and DOC, it was found that the use of a single or "pooled" regression to predict DOC resulted in the miscalculation of concentrations by more than 50 % as it failed to take account of the fact that the fraction of coloured DOC could vary by as much as 40 % on a spatial and temporal basis. Furthermore, the general ability of spectrophotometric analysis to measure low concentrations of DOC is ambiguous, as depending on the calibration used and thus the value of the intercept, the minimum amount of DOC detectable varies considerably and may be as high as 10.32 mg Cl^{-1}. Therefore, the spectrophotometric determination of DOC in soil water solutions generally has little discriminatory power to distinguish between carbon fractions, especially when pooled datasets are used, and is thus unsuitable for making accurate predictions regarding DOC flux in such environments.

CHAPTER 6

MICROBIAL ACTIVITY AND DOC PRODUCTION POTENTIAL IN DRAINED AND RESTORED BLANKET PEAT

6.1. INTRODUCTION

Peatlands are particularly unbalanced ecosystems in which the rate of production and accumulation of organic material far exceeds the rate at which it is degraded and exported (Frolking *et al.* 2001; Gorham 1991). This is generally a result of the low biodegradation rates that are often observed in these anoxic waterlogged soils, which result in slow biomass decomposition rates and allow a thick layer of peat to accumulate over many thousands of years (Freeman *et al.* 1996; Pind *et al.* 1994; Waddington *et al.* 2001). DOC production and release represents the balance between the release of DOC from organic matter, its exchange and sorption from particulate surfaces, its incorporation into microbial tissue, and its release via decomposition and respiration as CO_2 and CH_4 (Moore & Dalva 2001). In blanket peat soils, mobilised DOC enters a largely anaerobic medium, and under such conditions carbon is less likely to be metabolised to CO_2, and therefore substantial amounts of DOC accumulate (Freeman *et al.* 2004a). The anaerobic conditions also represent a potent constraint for oxygen-dependent enzymes such as phenol oxidase, one of the few enzymes able to degrade highly recalcitrant phenolic compounds, such as lignins and humic acids (Freeman *et al.* 2004a). Consequently, the accumulation of these phenolic compounds can suppress hydrolysis and microbial metabolism both in the peatland and its recipient stream waters.

Evidence about the role of water table drawdown on DOC production and export has provided contradictory results and has generally lacked any process-based information. However, it appears that drainage can result in a prolonged period of water table drawdown, which increases the level of oxygenation within the peat, with

Freeman *et al.* (2001b) identifying that when a peat is oxidised there is a stimulation of the enzyme phenol oxidase, which breaks down the inhibitory phenolic compounds and subsequently enhances the activity of degrading enzymes. Dehydrogenase is an oxidoreductase enzyme that takes part in respiration within microbial cells (Mosher *et al.* 2003). Consequently, any increase in the rate of dehydrogenase activity is indicative of a stimulation of microbial activity, which is likely to result in a greater oxidation of organic matter and thus elevated DOC production and ultimately CO_2 emissions from the peat (Silvola *et al.* 1996).

Nonetheless, the majority of research regarding the role of micro-organisms in response to environmental change comes from studies of mineral soils from well-drained forest, pasture and agriculture ecosystems (Fisk *et al.* 2003). Thus, we know relatively little about the micro-organisms existing in peatlands, with surprisingly few studies examining the influence of drainage on soil enzyme activity, despite the potential impact this may have on the global carbon cycle. Furthermore, it is currently unclear how the rate of microbial activity will respond to peatland restoration in the form of drain blocking, as although the re-inhibition of the hydrolase enzymes may occur in response to a rising water table, the rewetting of the peat may not necessarily reverse this process. This is because the reduction in phenolic compounds means it is possible for decomposition to continue at depth even after the water table has been restored – a process that has been referred to as the 'enzyme-latch' mechanism (Freeman *et al.* 2001a).

In order to assess the contribution of peatlands to the global carbon economy, we must improve our process-based understanding of how environmental change, with respect to drainage and restoration, alters the carbon production potential of the peat. Disturbance of soil microbial activity can serve as an estimate of ecosystem disturbance and thus the relative rate of carbon loss. Therefore, it is the aim of this chapter to establish whether disturbance in the form of drainage and drain blocking alters the rate of microbial activity and thus DOC/colour production. In addition, comparisons will be made between the organic matter and moisture content of soil samples in order to determine the influence of the varying land management techniques on the DOC production potential in a blanket peat soil.

6.2. METHODS

It was necessary to undertake fieldwork during the drier summer months when the water table would be at its lowest allowing for the greatest differences between sites to develop. At each of the three sites, fifteen soil samples were taken from depths of 0 cm and 20 cm within the soil profile. At the intact site, samples were taken across the entire length of the site and at a range of slope angles in order to remove the effect of any localised characteristics resulting from hillslope morphology. In contrast, at the drained and blocked sites all samples were taken from as close to the drain as was possible (~30 cm from the edge of the ditch) without destabilising the side walls, from both sides of the ditch. In addition, a second set of samples were collected from the drained and blocked sites; this involved measuring a 10 m transect across the drain on both sites and collecting soil samples from both depths (0 and 20 cm) from sites either side of the ditch that were spaced at 1 m intervals. In order to obtain a soil sample at 0 cm depth the covering vegetation was carefully cut back to reveal the soil surface, the subsurface sample depth was then measured from this exposed surface. At the intact and blocked hillslopes it was necessary to carefully dig soil pits, and samples were then taken from the pit walls to ensure that the soil had not been mixed during the excavation process. Once collected, the soil samples were placed in air tight bags and kept out of direct sunlight to ensure minimal disruption to the soils properties, which could be caused by oxidation or loss of moisture, and were refrigerated within 24 hrs of collection.

The measurement and comparison of rates of microbial activity across the three sites and between soil depths was investigated using the electron transport system (ETS) method proposed and described in full by Gammelgaard *et al.* (1992). It involved an enzyme assay to measure the concentration of dehydrogenase enzymes, which are found in all living organisms and take part in many reactions involving the transfer of electrons (Pepper & Gerba 2005; Tate 1995). Subsequently, as dehydrogenase enzymes take part in the electron transfer system of aerobic organisms, the activity of these enzymes is also a measure of respiration along with general metabolic activity (Frankenberger & Dick 1983; Pepper & Gerba 2005).

The enzyme assay was performed using an artificial electron acceptor created from the yellow coloured soluble tetrazolium salt INT [2-(*p*-iodophenyl)-3-(*p*-nitrophenyl) -5-phenyl tetrazolium chloride]. The assay involved incubating soil samples mixed with a solution of INT in an air-tight container to exclude oxygen, so that the INT could serve as the ultimate electron acceptor during respiration (Camina *et al.* 1998; Pepper & Gerba 2005). The reduction of tetrazolium salts has been used as an indicator for dehydrogenase activity for a wide range of microbes, ranging from bacteria to fungi and algae (Mosher *et al.* 2003). The exclusion of oxygen favours the transfer of the electrons to INT, and subsequently reduces the yellow compound to red INT-Formazan. After incubation, a solvent is added to the soil to extract the INT-Formazan, and its concentration is measured using absorption spectrophotometry at 480nm. Over a certain range of concentrations, the degree to which INT-Formazan absorbs 480nm light is a linear function of the concentration in the solution; therefore its concentration is determined using a standard curve developed from absorbance readings of standard INT-Formazan solutions (Gammelgaard *et al.* 1992).

The spectrophotometric assessment of the INT-Formazan samples was however, found to be affected by a significant amount of interference from the release of coloured humic substances, to such an extent that the expected red colouration was not visible to the naked eye. Subsequently, in order to remove the interference by the humic substances and thus ensure that only INT-Formazan concentration was being measured, the method of standard additions was applied, which involved the progressive spiking of samples with known quantities of red INT-Formazan and measuring the resultant level of absorbance at each interval. As the increase in absorbance with progressive spiking is assumed to be equal to the amount of standard added to the sample, it was possible to determine the concentration of INT-Formazan originating in the sample by plotting the volume of standard added on the x-axis against the level of absorbance (y-axis) and using linear regression to back predict the original value of INT-Formazan (Klein Jr & Hach 1977).

The moisture content of the peat soil samples was determined by filling a crucible of known weight with a field-moist soil sample, weighing it, placing it in an oven for 24 hours at 105 °C, and then re-weighing it. The moisture content was subsequently calculated by dividing the mass of the water lost over the mass of the oven-dried soil sample and is expressed as the gravimetric moisture content, which depicts the weight (in g) of water associated with 1 g of dry soil. Alternatively, the moisture content can be expressed as a percentage of the mass of the solid phase.

The simplest way of determining the percentage of soil organic matter is to burn it off and measure the loss in weight of the soil between drying at 105°C and ignition at 550°C. Thus, once the soil moisture content had been determined the samples were placed in to a muffle furnace set at 550 °C for a further 24 hours, and then reweighed. The organic matter content (OMC (%)) was then calculated in the following way:

OMC (%) = (Mass of oven-dry soil - Mass of ignited soil) x100 / Mass of oven-dry soil

As a complete dataset, using values taken from all three treatments, the moisture content and INT-Formazan data were found to be positively skewed. Therefore, a log transformation was used in order to normalise the data. The organic matter content data was found to be normally distributed, and thus did not require any transformation. Data were also checked for equality of variances before parametric tests of differences between treatments were applied, which included ANOVA and Student's t-test.

6.3. RESULTS

6.3.1. MICROBIAL ACTIVITY

As seen in Table 6.1, the concentration of INT-Formazan is higher at the drained site compared to the intact site, whilst the concentration at the blocked site is lower than that at both the drained and intact sites. The INT-Formazan concentration at the drained treatment was nearly double that of the blocked site, and this difference was found to be significant at $p < 0.05$. However, although the concentration of INT-Formazan at the drained site was 33 % higher than that observed for the intact site, and whilst the concentration at the blocked site was reduced by 31 % with respect to the intact treatment, both differences were not found to be significant at the 95 % confidence level (Figure 6.1).

The INT-Formazan concentration was higher at depth, with the average value at 20 cm elevated by approximately 18 % relative to 0 cm (Table 6.2). Nonetheless, as seen in Figure 6.2, when the depths of 0 and 20 cm were compared within sites, the differences were not found to be significant at $p < 0.05$ at any of the three treatments. However, when the same depths were compared amongst the sites, the drained site had a significantly ($p = 0.016$) higher INT-Formazan concentration at the surface (0 cm) than the blocked treatment. Further analysis was undertaken to determine whether the INT-Formazan concentration varied in either an up-slope or down-slope direction from the ditch or block, but again no significant differences were found when these areas were compared within sites. In addition, although when the up- and down-slope areas of the drained site were compared to the corresponding points at the blocked site the INT-Formazan concentration was found to be 50 % higher at the drained site, in both directions, this was not found to be significant ($p = 0.117$).

	Treatment								
	Intact			Drained			Blocked		
	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
INT-Formazan (µg l^{-1})	14.08	± 1.19	23	18.67	± 1.24	24	9.72	± 1.29	23
Moisture Content (g) *	6.87	± 1.06	23	6.65	± 1.03	24	6.77	± 1.06	23
Organic Matter (%)	96.49	± 0.19	30	97.39	± 0.14	30	95.19	± 0.48	29

* = (g H_2O g^{-1} dry soil)

Table 6.1 Descriptive statistics for the three treatments, including INT-Formazan concentration, moisture content and organic matter content, ± SE of the mean and sample size (n).

	Treatment								
	Intact			Drained			Blocked		
	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
INT-Formazan (µg l^{-1})									
0 cm	12.84	± 1.29	11	18.30	± 1.34	12	8.11	± 1.40	12
20 cm	15.32	± 1.29	12	19.05	± 1.40	12	11.84	± 1.50	11
Moisture Content (g) *									
0 cm	6.33	± 1.09	11	6.31	± 1.03	12	5.95	± 1.09	12
20 cm	7.40	± 1.07	12	7.02	± 1.04	12	7.79	± 1.06	11
Organic Matter (%)									
0 cm	95.88	± 0.27	15	96.97	± 0.19	15	94.53	± 0.67	14
20 cm	97.09	± 0.13	15	97.81	± 0.14	15	95.81	± 0.66	15

* = (g H_2O g^{-1} dry soil)

Table 6.2 Descriptive statistics for the three treatments by soil depth, including INT-Formazan concentration, moisture content and organic matter content, ± SE of the mean and sample size (n).

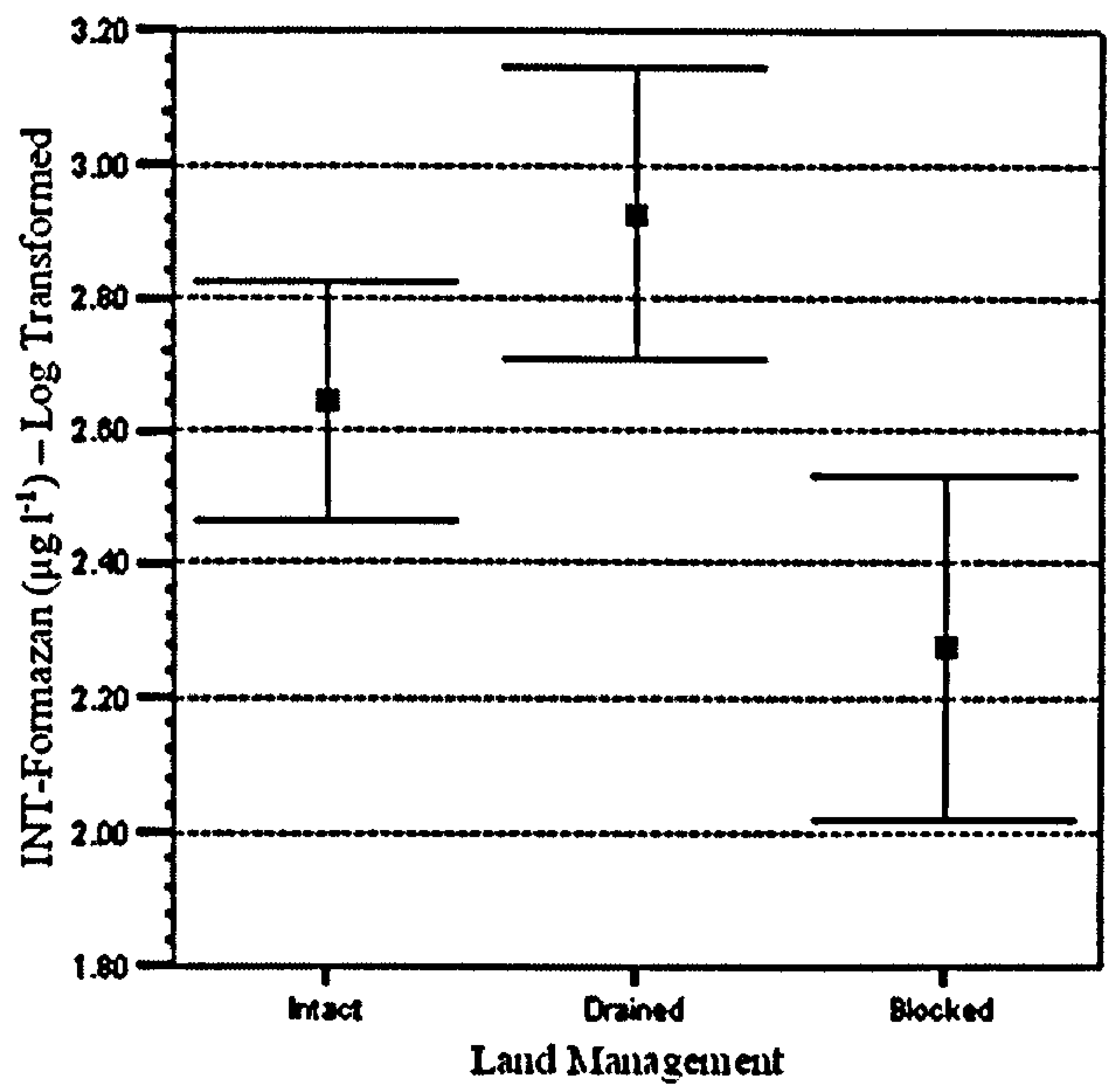


Figure 6.1 Mean INT-Formazan concentration for the three treatments, including ± 1 SE of the mean.

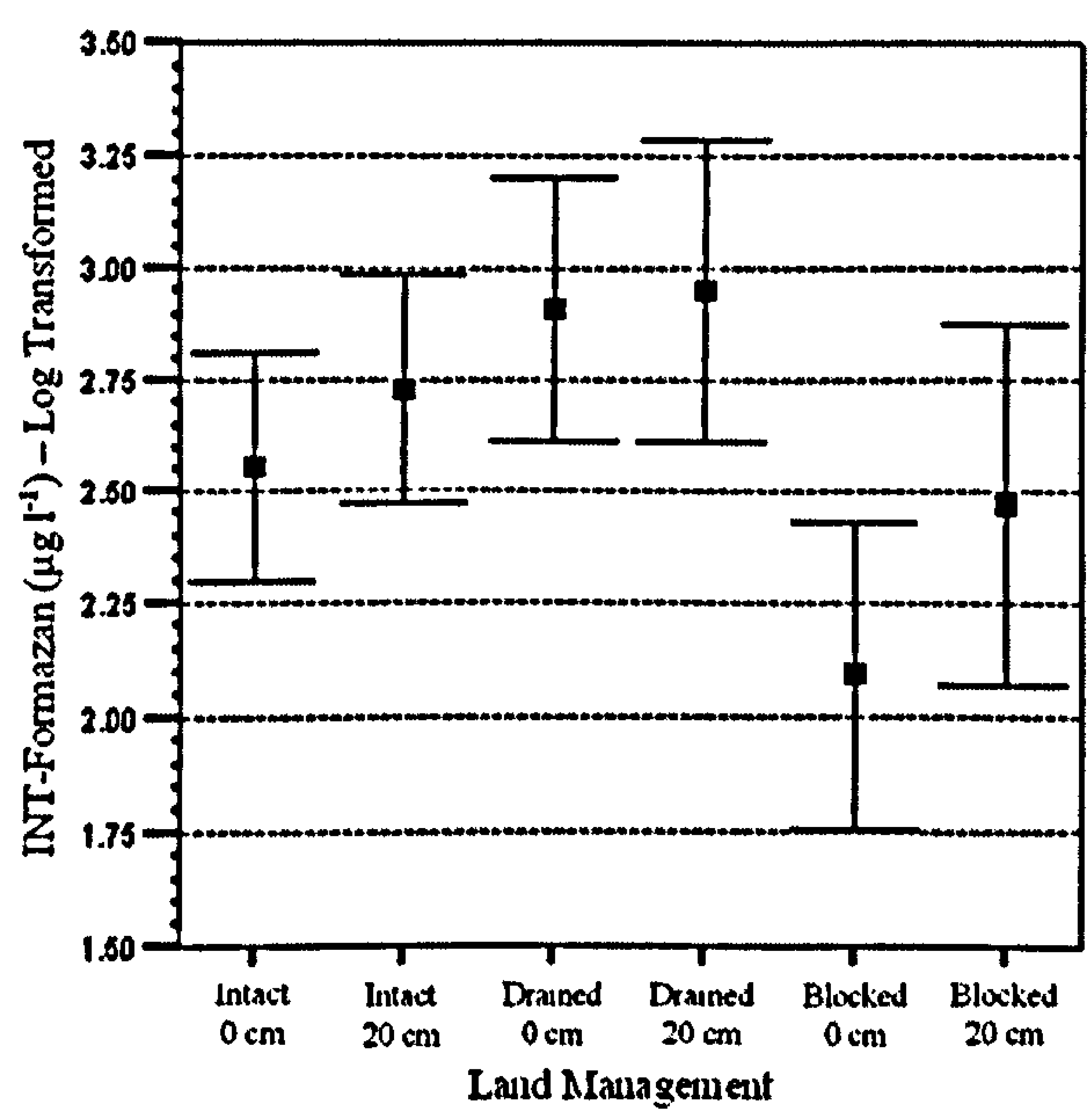


Figure 6.2 Mean INT-Formazan concentration by soil depth for the three treatments, including ± 1 SE of the mean.

6.3.2. ORGANIC MATTER CONTENT

When the amount of organic matter as a percentage of the soil mass was compared between land managements, significant (p <0.01) differences were found between all three sites, with drained > intact > blocked (Figure 6.3). Significant (p <0.002) differences were also found when the organic matter content was compared between the soil depths of 0 and 20 cm at the intact and drained sites, with the surface (0 cm) layer having a lower organic content than the deeper soil layer at 20 cm (Figure 6.4). However, at the blocked site, although the organic matter content at 20 cm was higher than that at 0 cm, the difference was not found to be significant (p = 0.093). When soil depths were compared amongst the three sites, the amount of organic matter was found to be significantly (p <0.003) higher at both 0 and 20 cm at the drained site compared to the intact site, and also when the drained site was compared to blocked treatment (p <0.01). The organic matter content seemed to be lower at both 0 and 20 cm at the blocked site when compared to the intact site, but this was not found to be significant (p = 0.08). Due to a lack of data, no comparisons in organic matter content could be made between the up-slope and down-slope areas of the drained and blocked sites.

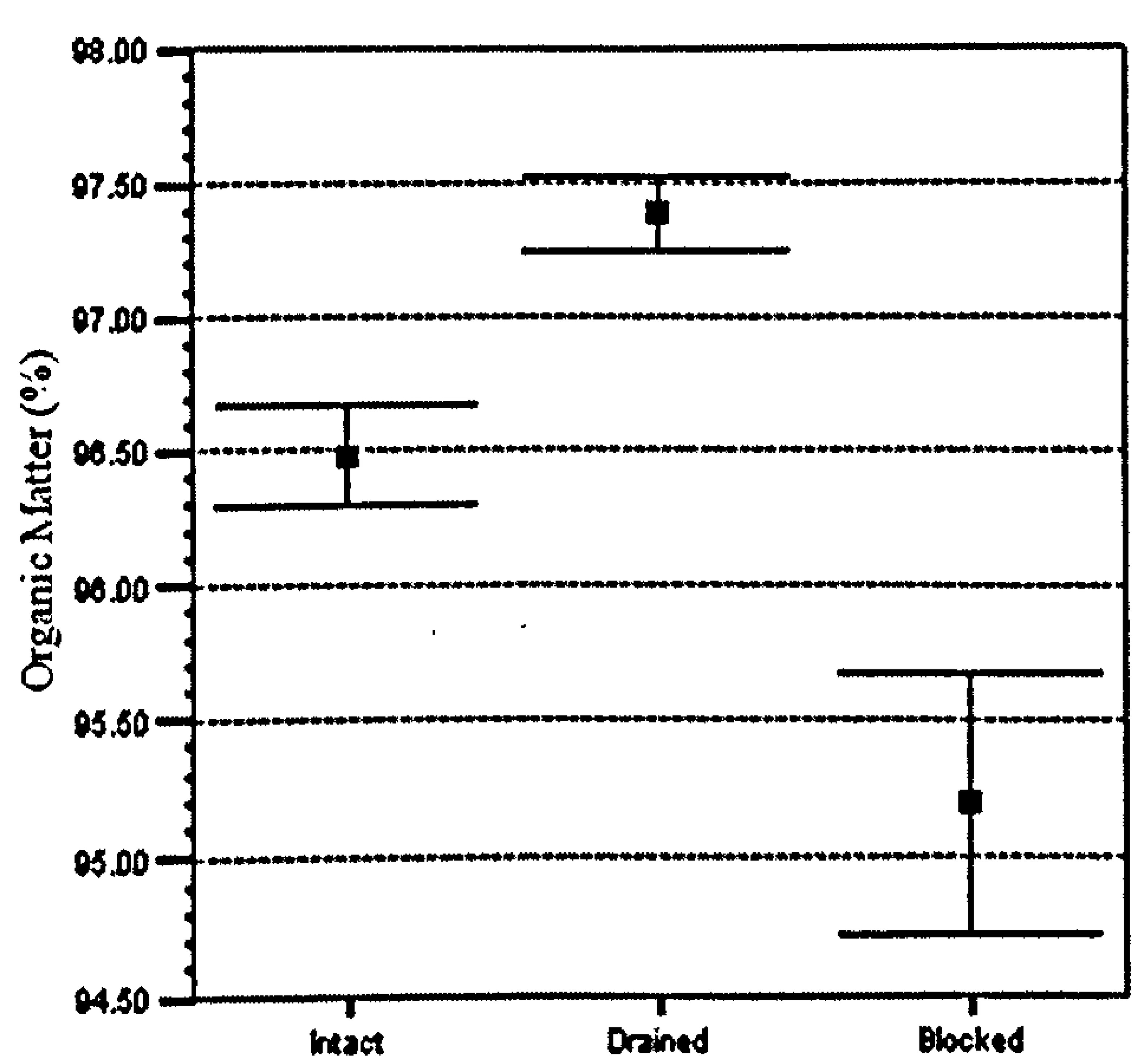


Figure 6.3 Mean organic matter content for the three treatments, including ± 1 SE of the mean.

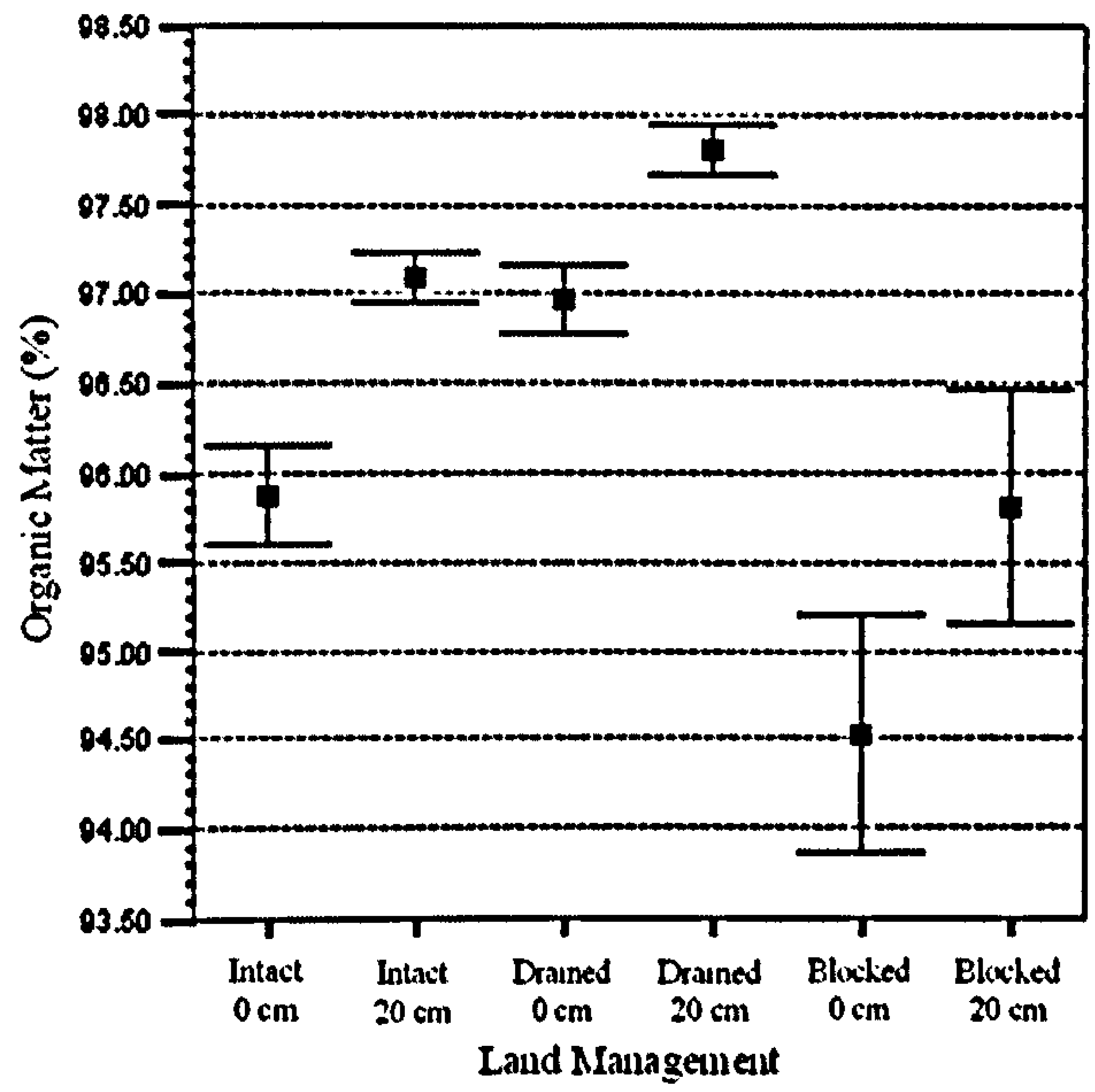


Figure 6.4 Mean organic matter content by soil depth for the three treatments, including ± 1 SE of the mean.

6.3.3. MOISTURE CONTENT

The assessment of Table 6.2 identifies that the level of moisture content was higher at the intact site compared to the drained and blocked sites, whilst at the drained site the moisture content was found to be lower than that of the blocked site, intact > blocked > drained. However, these differences between treatments were not found to be significant (Figure 6.5). In addition, Table 6.2 and Figure 6.6 identify that moisture content is higher at depth, with significant (p <0.05) differences observed between 0 and 20 cm at both the drained and blocked sites. At the intact site however, the difference in the moisture content observed between depths was not found to be significant (p = 0.08), and when the same depths were compared amongst sites, no significant differences were identified between any of the treatments. At the drained and blocked sites the moisture content appeared to be higher in the up-slope direction than down-slope, but this was not found to be significant (p = 0.174). Furthermore, when the up and down-slope areas of both sites were compared, the moisture content at the blocked site was found to be higher than the drained site, although again this was not found to be significant (p = 0.075).

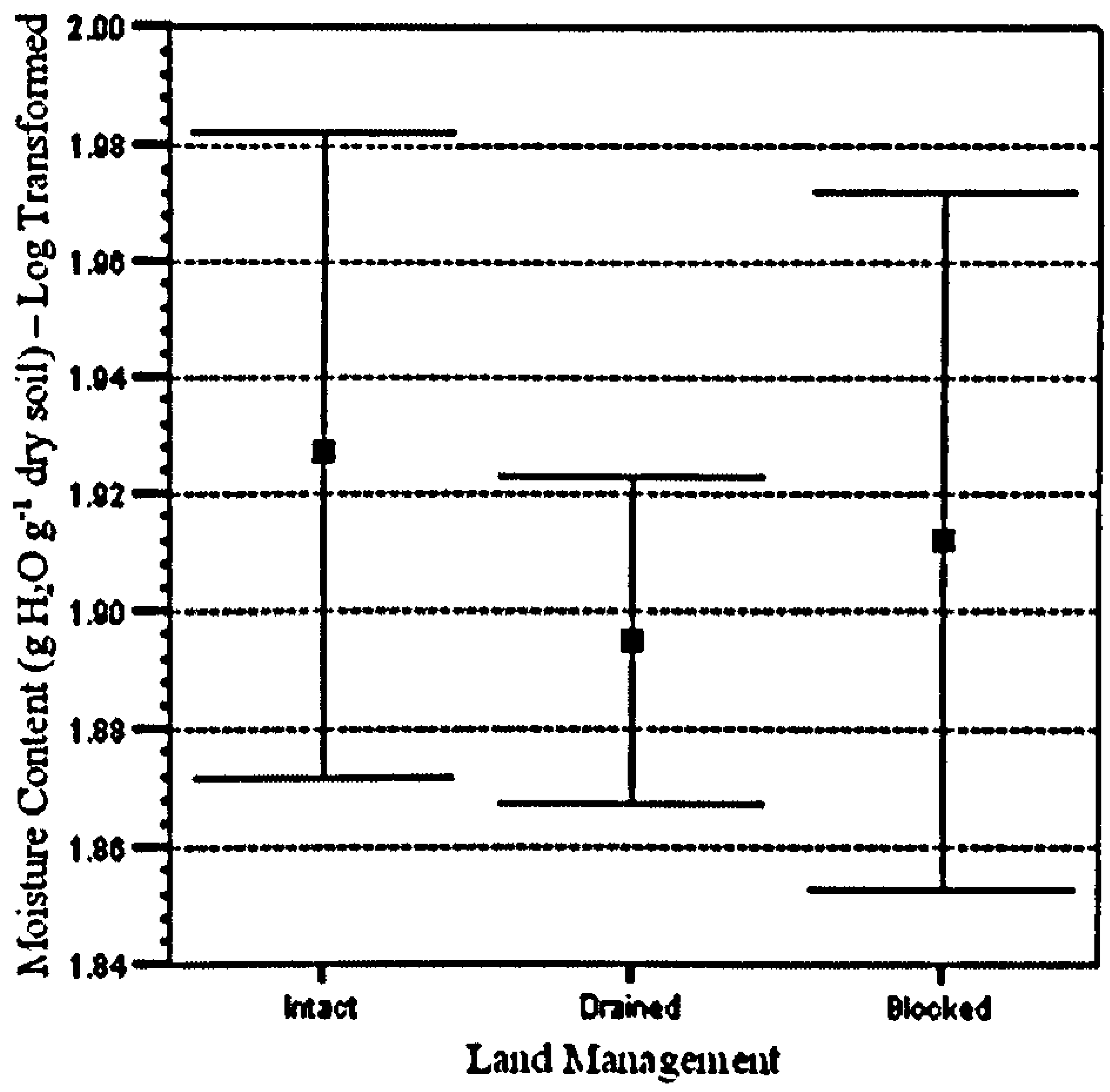


Figure 6.5 Mean moisture content for the three treatments, including ± 1 SE of the mean.

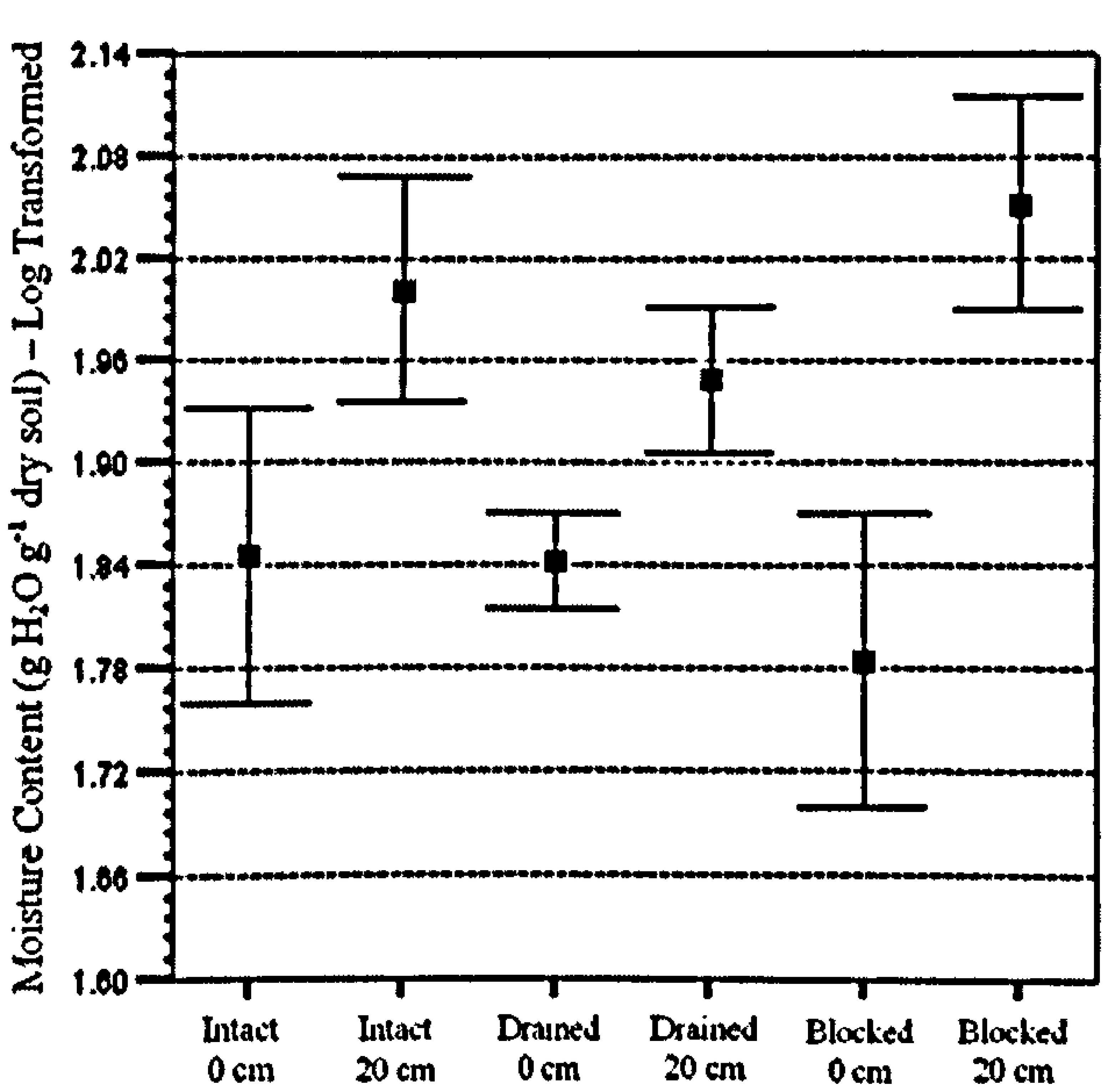


Figure 6.6 Mean moisture content by soil depth for the three treatments, including ± 1 SE of the mean.

6.4. DISCUSSION

Peat formation and development occurs through the production, decomposition and compression of organic matter derived from *Sphagnum* mosses and vascular plants (Clymo 1984). In undisturbed peat, the soils are normally devoid of molecular oxygen in all but the uppermost layer and thus enzymes such as phenol oxidase, which require molecular oxygen for their activity, are rarely active (Freeman *et al.* 2004b). In addition, the activities of enzymes, such as hydrolases that have no oxygen requirement, are also extremely limited in peatlands. Therefore, in undisturbed peatland soils levels of DOC and colour production are generally limited due to the high levels of inhibition faced by pivotal soil degrading enzymes.

Although the concentration of INT-Formazan observed at the drained treatment was found to be enhanced by 33 % relative to the intact site, this was not found to be significant at the 95 % confidence level. Therefore, it currently remains unclear as to whether the enhanced DOC concentrations and associated rise in the level of water discolouration experienced at the drained site occur in response to an enhanced level of microbial activity. However, it is thought that had the increase in microbial activity proved significant it may have occurred in response to a lowered water table, which would have increased the air-filled porosity of the peat and thus provided a greater rate of oxygen diffusion at depth. For example, Freeman *et al.* (2001b; 2004b) found that the low activity of degrading hydrolase enzymes was indirectly attributed to oxygen constraints on phenol oxidase, and that phenol oxidase activity increased 7-fold in response to oxygenation. Consequently, oxygenation appears to accelerate the aerobic microbial processing of soil organic matter, which is vastly more efficient than anaerobic respiration, and thus enhances DOC production. For example, Ingram (1978) found that anaerobic decay in the permanently waterlogged and anoxic catotelm occurs about a thousand times slower than aerobic decay in the periodically oxidised acrotelm above the water table; and Hogg (1993) found that if deep anoxic peat was exposed and aerated, that there was a 200-fold increase in the rate of CO_2 emission and mass loss from this material.

The apparent elevation of microbial activity at the drained site also corresponds well with the findings of Fenner *et al.* (2005) who assessed the hydrological controls on the diversity of phenolic degrading bacteria at Plynlimon, Wales. They observed consistently large increases in total phenol oxidase activities in response to simulated drought conditions, in line with the increase observed by Freeman *et al.* (2001b; 2004b) as a result of oxygenation. Fenner *et al.* (2005) suggested that since much of the peat matrix is composed of lignin, there could be profound implications of such increases in phenol oxidase activity with respect to intensified carbon losses because enhanced peat aeration (e.g. as a result of drought) has the potential to release greater concentrations of DOC to recipient aquatic systems due to the increased enzymatic mobilisation of the peat matrix.

The findings herein also support Hogg *et al.* (1992) who assessed the potential carbon losses from peat in response to enhanced temperatures, drought cycles and fire, and found that in a drained peat respiration rates increased as the peat became less saturated; and Lundquist *et al.* (1999) who observed higher respiration rates in soil exposed to wet-dry cycles, and suggested that this may be due to the utilisation of organic substrates that gradually build up as the soil is dried. Furthermore, Kuprevich and Shcherbakova (1971) found that radical changes in the hydrological regime stimulated phenol oxidase activity, and suggested that this was a result of increased aeration; and Dickinson and Dooley (1967) who found that un-drained basal peat was found to support small poplations of micro-organisms, with restricted activity due to the unfavourably wet soil conditions, yet when the soil was dried, microbial activity was found to increase due to the larger surface area of exposed peat. Finally, McDonald *et al.* (1991) found that colour production was maximised in a narrow acidic pH range and was very limited when temperatures were in excess of 45°C, and suggested that this ultimately reflected the production and activity rates of decomposing soil enzymes, such as hydrolases and desmolases, that are produced by soil bacteria.

In contrast, Freeman *et al.* (1995a) found that a drawdown in water table resulted in a suppression of microbial activity, rather than the anticipated stimulation, and Freeman *et al.* (1996) found that the level of respiratory activity in a drought-induced peat bog was not significantly different to the control, nor was the level of inhibitory phenolic compounds. Furthermore, Williams *et al.* (2000) studied phenol oxidase activity in two *Sphagnum*-dominated peatlands during a strong summer drought in order to determine how it varied in response to changes in water level and aeration. They found that the level of phenol oxidase activity did not vary significantly during the drought period, and did not differ as a function of depth, sample date or with water-table depth. Nonetheless, they did find an exponential increase in phenol oxidase activity with increasing pH. Subsequently, Williams *et al.* (2000) suggested that the low phenol oxidase activity was a result of an enzyme inhibitory effect by compounds derived from the vegetation, and that a persistent drought may be required to bring about the necessary changes in aeration and pH before phenol oxidase activity can increase.

Further evidence to support the finding of enhanced microbial activity and thus DOC production at the drained site was seen in the significantly higher levels of organic matter, which indicate there is a greater amount of material available for micro-organisms to produce DOC relative to the intact site. Such a finding is, however, counter-intuitive given that when a peat soil is drained, it is thought that the organic matter would be decomposed faster in response to the elevated rates of microbial activity, and thus the organic matter content at the drained site should be lower than the intact site. For example, Fleck *et al.* (2004) found that peat that had been drained for agricultural production in the Sacremento-San Joaquin Delta California had become heavily oxidised in the top soils layers and resultantly had reduced carbon content compared to more intact wetter peat nearby.

However, soil organic matter is actually composed of plant and animal remains in various stages of decomposition, cells and tissues of soil organisms, and substances from plant roots and soil microbes, and its amount is controlled by a balance between additions of plant and animal material and losses by decomposition, which are both strongly controlled by management activities (USDA 1996). Thus, it is thought the higher organic matter content observed at the drained site may be a result of enhanced plant biomass and/or enhanced microbial biomass given that i) the drained site has been shown to support a heightened level of microbial activity and Nielsen and Winding (2002) found that although the biological components of peat occupy a tiny fraction (<0.5 %) of the total soil volume, they make up as much as 10 % of the total organic matter; and ii) the water table drawdown may have increased the amount of more woody, vascular plants relative to amorphous *Sphagnum* moss. Belyea and Clymo (2001) found that litter and thus organic matter production increased with acrotelm thickness mainly due to enhanced production by vascular plants.

Although the soil moisture content appeared to be reduced at the drained treatment relative to the intact and blocked sites, particularly in a down-slope direction suggesting that the drains may actively divert moisture away from the peat, these results were not found to be significant at the 95 % confidence interval. Therefore, it currently remains unclear as to whether the proposed lowering of the water table associated with drainage results in the de-saturation of the surface peat. Nonetheless, the apparent direction of change in moisture content levels does relate well to the findings of McDonald *et al.* (1991), Prevost *et al.* (1997) and Price (1996) who all observed lower moisture content levels in cutover and drained peats compared to natural peatlands. It is thought the reduction in moisture content is a result of the lowered water table causing dewatering from the large diameter pores with low suction pressure, with Burke (1967) noting that in drained catchments where the water table had been reduced there was subsidence, which was attributable to the shrinkage caused by the soil dewatering.

The reduction in soil moisture content and associated rise in microbial activity also corresponds well with the findings of McDonald *et al.* (1991) who found that the rate of production of decomposition products is dependent upon soil moisture status, and that colour accumulates during periods of soil moisture deficit when water movement is not sufficient to move it out of the soil profile. They found that the drying of peat results in the dewatering of soil pores and promotes a faster rate of aerobic decomposition by exposing the peat to aerobic bacteria and oxidation processes, and that prolonged drying overcomes the high suction moisture pressures found in smaller pores and thus greatly increases the surface area upon which aerobic decomposition processes can act. Thus, effectively changes in peat moisture content can expose new substrate upon which renewed microbial activity can take place, with Orchard *et al.* (1992) finding a positive relationship between respiration rates and gravimetric water content.

The INT-Formazan concentration at the blocked site was found to be significantly lower than that of the drained site, which shows that the reduced levels of DOC and water discolouration observed at the blocked site in Chapter 4 are the result of a much lower level of microbial activity and therefore DOC production. This is, however, contrary to Freeman *et al.* (2001b) who suggested that the loss of inhibiting phenolic compounds (in response to enhanced phenol oxidase activity associated with oxygenation and water table drawdown) means that it is possible for decomposition to continue at depth even after the water table has been restored. Thus, in the long-term at least, there is no evidence that drain blocking is associated with the theorised enzyme-latch reaction, in which it was hypothesised that enzymes are 'switched on' by water table drawdown but are not 'switched off' as the water table recovers.

The reduction in microbial activity at the blocked site appears to be in response to a re-saturation of the peat, which when taken in conjunction with the higher moisture content at the blocked site compared with the drained treatment, particularly in the down-slope direction, is indicative of a successful water table restoration. However, if this was the case, it is difficult to understand why the blocked site has a lower level of microbial activity than the intact site (albeit non significant). In addition, the moisture content at the blocked site was found to be lower than the intact site, which indicates that although the water table may be restored, it is likely to be more variable and/or generally lower than the intact site. This enhanced level of variability may have resulted in a flushing of the porewaters, and the preferential removal of the more labile components, as well as a subsequent alteration to the level of decomposition; such that although there is a reduced level of DOC produced due to microbial inhibition, there is ongoing consumption and turnover of existing organic matter and thus a reduction in litter quality. This is evident by the reduction in organic matter content at the blocked treatment relative to the drained and intact sites, as well as the reduced DOC concentrations, E4/E6 ratio and the enhanced C/C ratio observed in Chapter 4, and the altered colour – carbon relationship in Chapter 5.

The lower microbial activity and thus DOC production rates at the blocked treatment compared to the intact site is characteristic of an older, more degraded peat, whose labile carbon compounds have been consumed over time by microbes (Updegraff *et al.* 1995). In addition, the decrease in DOC and colour production may be due to the accumulation of compounds unfavourable to microbial activity, such as lignins and phenolics, as substrate quality is a major factor influencing the rate of decay (Hogg *et al.* 1992; Updegraff *et al.* 1995). For example, Bridgham and Richardson (1992) and Yavitt *et al.* (1987) found that the poor substrate quality of highly decomposed, humified peat limits both CO_2 and CH_4 production rates, even though peat is 95 % organic matter; whilst Bossio and Scow (1995) studied the impact of carbon and flooding on the metabolic diversity of microbial communities and found unique substrate utilisation patterns in flooded versus drained agricultural soils, and suggested that there were different DOC compounds in saturated soils than in soils subjected to seasonal drought.

In addition, Tipping *et al.* (1999) identified that the activity of the microbial community decreases when there is an exhaustion of a finite pool of soil organic matter available for transformation into potentially mobile forms; whilst Clymo (1965) and Belyea (1996) showed that slow decay rates were due primarily to water table position, but also to a decline in litter quality with peat age; and Hogg (1993) identified there to be an inverse relationship between the level of peat humification and the rate of microbial decay, which suggests organic material becomes more resistant to further decay as it decomposes.

Therefore, microbial processes also play a central role in the transformation and degradation of DOC, often in conjunction with physiochemical processes such as adsorption in soils or photochemical reactions in water. Furthermore, an important distinction between metabolism in anaerobic versus aerobic environments is that, under reducing conditions, organic matter is degraded by a multi-step process involving a consortium of bacteria (Fenchel & Finlay 1995). In anoxic peat, reactive components of organic matter are re-mineralised by stepwise degradation beginning with hydrolysis to form DOC. Then DOC undergoes fermentation and is transformed into volatile fatty acids such as acetate. Finally, the fermentation products are converted into CO_2 and CH_4 by sulfate reducing and methanogenic bacteria in a process known as terminal metabolism (Fenchel & Finlay 1995). However, this relatively simple linear model of degradation may be complicated by processes that produce recalcitrant organic substrates or promote the degradation of less reactive compounds (Hee *et al.* 2001). For example, the introduction of fresh organic material may stimulate the degradation of un-reactive or "relic" DOC via a mechanism known as co-metabolism or priming, which involves the microbial oxidation of substances without the utilization of the derived energy for growth (De Haan 1992; Hee *et al.* 2001). Furthermore, some of the compounds produced may be resistant to further degradation due to their inherent stability or as a result of abiotic reactions that protect the molecule from enzymatic attack (Hee *et al.* 2001).

The significantly lower organic matter content at the blocked site compared with both the drained and intact treatments shows that there has been significant degradation and removal of the carbon store, which corresponds well Kalbitz and Geyer (Kalbitz & Geyer 2002) who identified that because DOC release depends on soil organic matter content, if the soil layers have been degraded in any way there will be less available organic matter to produce DOC. Furthermore, the low E4/E6 ratio in conjunction with the high C/C ratio at the blocked site identified in Chapter 4 indicates that the smaller, more labile organic material has been removed, and shows that the organic matter is of low substrate quality. Thus, it is thought the re-saturation of the peat layers in response to a rising water table may have caused a flushing of porewaters that resulted in DOC becoming limited in supply. This may have then initiated a process of store exhaustion and/or priming whereby soil microbes act to continually breakdown existing organic material, which results in the development of older more decomposed and decay resistant organic material relative to the intact site.

Although the INT-Formazan concentration appeared to be greater at 20 cm depth relative to 0 cm at all three treatments, this was not found to be significant at the 95 % confidence level. However, had there been sufficient evidence it is thought that a greater rate of activity at depth may relate to the location of the water table within the soil. For example, Belyea (1996) found that although peat lost mass most slowly below the water table, the highest mass losses were in or slightly above the zone of water table fluctuation; and Tate (1980) found that peat soils experiencing alternating periods of anaerobic and aerobic conditions have higher organic matter oxidation rates than peats with constant moisture levels. In addition, Lahdesmaki and Piispanen (1988) and Williams *et al* (2000) found that phenol oxidase activity increased with peat depth, whilst Kravchenko and Doroshenko (2003) found that nitrogen-fixing activity in a raised bog was highest in the 10 to 20 cm layer of soil, and much lower in the upper and deeper (20 to 30 cm) soil layers.

These findings are, however, are in contrast to those of Pind *et al.* (1994) and Freeman *et al.* (1995b) who found that enzymatic activity decreased with increasing soil depth, and Fisk *et al.* (2003) and Yavitt *et al.* (1987) who indicated that surface peat generally supports a greater level of microbial activity because subsurface peat is older, more highly decomposed and should be less energetically favourable for microbial utilisation. However, it is thought that these inconsistencies may be a function of varying peat types and the individual environmental differences in each peatland and the resulting microbial community, and also because different groups of bacteria peak in different depths within the peat, often in relation to the position of the water table. For example, although the relative proportions of anaerobic to aerobic bacteria change with depth relative to the water table, anaerobic organisms can be found above the water table and aerobic organisms below due to the presence of pockets of oxygen in the upper saturated levels and anaerobic micro-sites above the water table (Charman 2002; Schiff *et al.* 1998). Thus, where the water table fluctuates most markedly, particular communities are present where the organisms are either facultative or are at least able to survive fluctuating aerobic/anaerobic conditions. Consequently, as maximum decay rates often occur around the position where the water table fluctuates the most, rather than in the fully aerobic zone, the higher INT-Formazan concentrations at 20 cm may be indicative of an established and more active microbial community at this depth relative to the surface.

As expected, organic matter and moisture content increased significantly with depth at the drained and blocked sites, which shows that the deeper soil layers are increasingly anoxic and thus accumulate more organic material due to the greater compaction and saturation relative to the surface layers. For example, Belyea & Clymo (2001) observed that each year's cohort of litter undergoes aerobic decay and is subsequently buried under the weight of younger material, until eventually the main plant structures collapse. This decreases the size of the soil pore spaces and thus reduces the hydraulic conductivity of the peat, which causes the water table to rise and results in the remaining plant material becoming submerged by the rising permanently waterlogged catotelm (Clymo *et al.* 1998). At the intact site, although organic matter and moisture content increased with depth, no significant differences were identified between soil depths. This is thought to indicate that the water table is much closer to the surface in the undisturbed peat and thus resultantly there is slightly less variability in these soil properties as the higher levels of saturation and anoxia result in a relatively more homogenous soil profile compared to the drained and blocked sites.

As previously described, the method proposed by Gammelgaard *et al.* (1992) that was undertaken to determine the concentration of INT-Formazan in soil samples, incurred a significant degree of interference due to the release of coloured humic substances that are characteristic of peat soils. Although a range of measures were applied to try and improve the efficiency of the technique and remove the interference, the low level of precision, in conjunction with a relatively low (<30) sample size, meant that some of the differences observed proved to be insignificant when tested at the 95 % confidence level. In addition, however, although Gammelgaard *et al.* (1992) noted there to be some interference caused by these humic substances, they made no direct attempt to correct for this, nor did they try to determine the influence it would have on the accuracy and precision of the method and subsequent results. Therefore, it is suggested that their results should be treated with a degree of caution, as should those reported from successive research that has used this method of analysis for peat soils and not corrected for this high degree of interference.

6.5. CONCLUSION

At the drained treatment, there appeared to be an enhanced rate of microbial activity and a reduced level of soil moisture relative to the intact site; however, this proved to be insignificant at the 95 % confidence level. Thus, it currently remains uncertain as to whether the elevated levels of DOC and colour observed in Chapter 4 occur as a result of stimulated microbial activity in response to enhanced oxygenation following water table drawdown. Nonetheless, a significant increase in organic matter content was observed at the drained treatment relative to the intact site, which indicates there is a higher DOC production potential at the disturbed site. It is thought that this increase in organic matter may be the result of enhanced growth in microbial and/or vegetative biomass in response to a greater level of aeration.

In contrast, significant reductions in the rate of microbial activity and organic matter content were observed at the blocked site relative to the drained site, whilst the moisture content was found to be enhanced. This suggests that blocking may have resulted in a relatively successful water table restoration and re-saturation of the peat, and therefore reduced DOC and colour levels by limiting their production potential via inhibiting microbial activity within the soil. In addition, it provides evidence against the commonly quoted hypothesis that an enzyme-latch reaction may be sustained in peat soil that has been re-wetted. The level of microbial activity, organic matter and moisture content at the blocked treatment all appeared to be lower than those observed for the intact site; however, this proved insignificant at the 95 % confidence level. Nonetheless, it gives some indication that although the water table may be restored, it may be more variable and/or generally lower than the intact site. Furthermore, it suggests that the reduced and somewhat modified DOC observed at the blocked site in Chapter 4 may relate to a store exhaustion/priming mechanism whereby there is a sustained rate of consumption and turnover of existing organic matter, which results in a reduction in litter quality and the inhibition of further microbial activity.

Many of the observed differences between sites provided in this chapter proved statistically insignificant. This is thought to be a result of the relatively low sample size and the fact that the spectrophotometric method undertaken for the measurement of microbial activity incurred a low level of precision. Therefore, although these results go some way to helping decipher the processes responsible for i) the elevated DOC and water discolouration observed at the drained site, and ii) the reduced yet heavily modified DOC released from the blocked treatment, there is clearly a need for further research and methodological development before we can accept such hypotheses.

CHAPTER 7

RUNOFF PRODUCTION AND HYDROLOGICAL CONTROLS IN DRAINED AND RESTORED BLANKET PEAT

7.1. INTRODUCTION

Peatland soils are of great hydrological significance within the UK given that the headwater catchments of many of the country's major river systems drain areas of upland blanket peat (Evans *et al.* 1999). As blanket peat generally consists of an anaerobic, heavily waterlogged, organic-rich soil, the high water table often results in over 80 % of runoff being produced as saturation-excess overland flow as the soil has only a limited rainfall storage capacity (Holden & Burt 2003c). Consequently, runoff production in undisturbed blanket peat catchments is typically termed "flashy" as they are very productive during storm flow events, exhibiting relatively short lag times between peak rainfall and discharge and thus high storm runoff efficiencies, yet they only provide minimal contributions to base flow (Bay 1969; Evans *et al.* 1999). The hydrological processes operating on blanket peat hillslopes range in scale from the dominating surface saturation-excess and infiltration-excess overland flow through to subsurface flow within the soil matrix, and via macropores and natural soil pipes. However, the runoff processes are not independent of each other and water travelling over the surface as overland flow at one point may later take the form of subsurface flow through the soil matrix and macropores, and their relative importance is known to vary depending on water table depth in conjunction with antecedent conditions and topographic position (Holden & Burt 2003b; Wallage *et al.* 2006).

Peatland hydrology is also fundamental to its own development and sustainability as it influences processes such as gas diffusion rates, redox status, nutrient availability and cycling, species composition and diversity (Holden 2006). As a result however, peatlands are highly sensitive to the changes in hydrology that often occur as a result of changes in climate or land management; factors which are likely only to intensify in future years (Bragg & Tallis 2001; Heathwaite 1995). Therefore, it is extremely important to be able to determine the effects of water table disturbance on the different forms of surface and subsurface flow given the fact that the various runoff production pathways act to attenuate and delay water movement through and across the peat to differing extents, and also provide significant transport routes for nutrient and sediment fluxes (Burt 1996). For example, it is possible that water table drawdown could significantly alter both the structural and infiltration properties of the soil and thus the hydrological routing of water through and across the peat, such that the individual runoff production processes are modified and alternative sources of DOC/colour are made accessible.

However, despite the significance of blanket peat catchments to upland hydrology, there has been a distinct lack of research in such environments, due in part to the logistical difficulties of obtaining data in remote upland catchments and also the technical difficulties associated with plot-scale investigations (Evans *et al.* 1999). Consequently, little is known about the effects of drainage and drain blocking on water table depth and processes such as infiltration and water movement in blanket peat soils, and how modifications made to these mechanisms influence runoff production and subsequently the hydrological routing of DOC and colour through and across the peat. Therefore, as identified in Objective 5 of Section 1.2, this chapter aims to determine whether the elevated levels of DOC, water discolouration and microbial activity observed at the drained site in the preceding chapters are the result of a greater level of aeration due to a lowered water table, and subsequently whether this has any influence on the structural and infiltration properties of the soil including overland flow generation, macroporosity, hydraulic conductivity and bulk density. In addition, this chapter will also determine whether the reduced levels of microbial activity and DOC/colour production associated with drain blocking observed in Chapters 4 and 6 are the result of a successful water table restoration, and identify how this influences the various structural and infiltration properties of the soil, as identified above.

7.2. METHODS

The water table is the level at which water pressure is equal to atmospheric pressure, and thus is the level at which open water will stand in a well that is hydraulically connected with the groundwater body (Gilman 1994). Accordingly, water table depth was monitored using a network of PVC dip-well tubes, which were installed along the length of the transects located at each site, with the depth to the water table in each dip-well being measured manually on a monthly basis by inserting an electronic dip-probe into the tube that had a water-sensitive sensor at its tip. When the sensor came into contact with the water, the dip-probe emitted a high-pitched buzzing sound and the length of the rod inserted into the tube before reaching the water could be determined, with measurements precise to the nearest 5 mm. In addition, due to the potential for movement of the tubes relative to the peat surface, constant records of the tube heights above ground were also taken to ensure that the depth to the water table was accurately measured.

The manual readings were used to calibrate automated pressure transducers, which recorded the water level in the dip-well every 20 minutes over the sample period December 2004 to July 2006, and were located in nine of the wider dip-wells along one of the transects at each site. Three pressure transducers at each site were located in an up-slope direction and spaced at distances of 1 m, 2 m and 15 m from the ditch, whilst six were located at positions 1 m, 2 m, 3 m, 14 m, 24 m, and 34 m from the ditch in a down-slope direction (or equivalent at the intact site). However, it became apparent that one of the pressure transducers at the blocked site (positioned 1 m up-slope) had recorded rather unreliable and inconsistent water table results relative to the other eight that were located at the site. Therefore it was decided that, in order to produce the most reliable results, it would be best to remove the data from this transducer and in order to provide a valid comparison between sites data from the corresponding point located along the intact and drained transects was also excluded from further analysis.

The generation of overland flow at each site was monitored using a network of fourteen crest-stage tubes that were installed along each of the two transects located at each site. The crest-stage tubes had flow entry points located relative to the surface of the peat, so that any flow or ponding of water on the surface resulted in the filling of the tube with water (Holden 2000). This provided a means of monitoring the potential for OLF generation as it allowed for the assessment of the number of times during the study period that OLF occurred in between the monthly sampling sessions, as the user records whether any water has entered the tube since it had been extracted for chemical analysis during the previous months sample session.

Macroporosity and hydraulic conductivity were determined using a mini-disk tension infiltrometer, which provides a rapid and convenient method for obtaining a large amount of field infiltration data, and has been recognized as being a reliable and useful tool for the *in-situ* determination of saturated and near saturated hydraulic properties, as well as soil structural conditions at and near the soil surface (Azevedo *et al.* 1998; Baird 1997; Zhang *et al.* 1999). However, to date only a limited number of studies have used tension infiltrometers on peat soils (e.g. Baird 1997; Holden *et al.* 2001). Tension infiltrometers measure infiltration rates at water pressures which are negative with respect to atmospheric pressure (Jarvis *et al.* 1987). In this way, the pre-ponding conditions characteristic of the early stages of rainfall can be simulated as the tension infiltrometer allows infiltration of water into the soil matrix, but does not allow flow into larger macropores that may otherwise dominate the infiltration process and short-circuit the flow (Holden *et al.* 2001; Jarvis *et al.* 1987).

Although definitions of macropores vary widely and the choice of an effective size to delimit macropores is arbitrary, Luxmoore (1981), Watson and Luxmoore (1986) and Baird (1997) all use the value of -3 cm tension to distinguish between macropores that drain at field capacity and smaller meso- and micropores, which according to capillary theory indicates that macropores are >1 mm in diameter (Luxmoore *et al.* 1990). By maintaining the supply head at a range of negative pressure values it is possible to determine the role of macropores and meso/micropores during infiltration, as by subtraction, the hydrological role of the larger pores during the infiltration process can be evaluated (Casanova *et al.* 2000; Jarvis *et al.* 1987). For example, since capillary pressure can be related to an equivalent pore diameter, the difference in infiltration rates between two differing tensions can be associated with the pore classes defined by the tension range, with the proportion of field saturated hydraulic conductivity governed by macropores being calculated by subtracting the infiltration rate at -3 cm tension from the field saturated hydraulic conductivity (Baird 1997).

Measurements were undertaken during the month of July 2005 when it was thought that the water table would be at its lowest allowing for the greatest differences between sites to develop, and to comply with the assumption that the unsaturated hydraulic conductivity of the soil prior to the test is significantly lower than the hydraulic conductivity under the imposed infiltration conditions (Baird 1997). A total of 14 infiltration experiments were conducted at each hillslope. Sample locations at the intact site were chosen at random across the entire length of the hillside and at a range of slope angles in order to remove the effect of any localised characteristics resulting from hillslope morphology. In contrast, at the drained and blocked sites, sample points were chosen as close to the drain as possible and on both the up- and down-slope sides, with a selection of drains sampled on each hillslope in order to reduce the level of error that may be associated with an individual ditch.

At each sample-point location vegetation was carefully cut back to the peat surface and any surface irregularities were removed with a serrated knife, before a layer of moist fine sand of the same diameter as the circular base of the infiltrometer was applied to smooth out any remaining irregularities at the soil surface and improve the contact between the disk and soil surface (Baird 1997; Holden *et al.* 2001). Moist sand was used as it maintains good hydraulic connectivity but does not fall down into surface-vented macropores forming 'wicks' as would air-dry sand (Messing & Jarvis 1993). The infiltrometer was then placed on the sand. As the supply reservoir of the mini-disk infiltrometer was small, the total volume of water held in the instrument was low, which not only reduced the likely chance of soil compression, but also aided accurate measurements of discharge (Holden *et al.* 2001).

Infiltration measurements were performed at tensions of -1 cm -3 cm and -5 cm, and were conducted using the lowest supply head (-5 cm) first, as reversal may lead to hysteresis where drainage occurs close to the disk while wetting continues near and at the infiltration front (Reynolds & Elrick 1991). Infiltration measurements continued until a steady state was achieved, and the instrument was shaded in order to reduce sunlight heating of the supply reservoir (Baird 1997). Hydraulic conductivity rates were obtained from the steady-state infiltrometer data using the method outlined by Reynolds and Elrick (1991) and as performed by Baird (1997) and Holden *et al.* (2001), whereby Wooding's (1968) solution for infiltration from a shallow pond is combined with Gardner's (1958) unsaturated hydraulic conductivity function.

Bulk density, defined as the mass of a unit volume of undisturbed dry soil, is a particularly important measurement as it gives an indication as to the degree of compaction and decomposition of a soil and also provides an indication of the ease by which plants roots can penetrate, with soils having a high proportion of pore space to solids exhibiting the lowest bulk densities (Brady & Weil 2002). Bulk density is also closely related to pore-size distribution, which helps regulate water retention and saturated and un-saturated water transport dynamics in peat soils (Boelter 1964; 1969; 1972). During the drier summer months, a total of 24 soil samples were collected from each of the three sites, and consisted of six samples taken from depths of 5, 10, 20 and 40 cm within the soil profile. In contrast to the sampling strategy undertaken for the infiltration experiments, bulk density soil samples were taken from various points located along the length of one transect from each site. Samples were collected by carefully digging soil pits and extracting the soil at the relevant depths from the pit walls to ensure that its structure had not been disturbed during the excavation process. Once collected, the soil samples were placed in air tight bags and kept out of direct sunlight to ensure minimal disruption to the soils properties, which could be caused by oxidation or loss of moisture, and were refrigerated within 24 hrs of collection. Bulk density measurements were carried out in the laboratory by recording the weight of oven-dried soil required to fill a measuring cylinder of known volume, and was calculated by dividing the weight of the soil by the volume of the cylinder to give a value in g cm^{-3}.

Initial assessment of the complete dataset, using values from all three treatments, identified that water table depth, occurrence of OLF, percentage macropore flow, hydraulic conductivity and bulk density were all normally distributed, and thus required no transformations. Data were also checked for equality of variances before parametric tests of differences were applied that included ANOVA and Student's t-test, whilst parametric tests of association between variables was carried out using Pearson's correlation coefficient.

7.3. RESULTS

7.3.1. WATER TABLE

Analysis of variance of the mean daily water table depth identified significant (p <0.001) differences between all three sites (Figure 7.1, Table 7.1). Further assessment revealed that whilst drainage had significantly (p <0.001) reduced the mean daily height of the water table by approximately 10 cm to -13.87 cm relative to the intact site, and drain blocking had been successful in causing a significant (p <0.001) rise in the height of the water table to -9.30 cm relative to the drained site, the mean daily depth at the blocked site was still significantly (p <0.001) lower than that of the intact site (-4.25 cm). Although the drained site exhibited the greatest maximum water table depth of -27.29 cm, which was nearly double that observed at the intact site (-13.87 cm), the maximum depth recorded at the blocked site (-20.10 cm) was still 50 % lower relative to the intact site.

Water Table Depth (cm)	Treatment								
	Intact			Drained			Blocked		
Dip-well Station	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
1 (15 m US)	-4.90	± 0.15	564	-12.69	± 0.21	564	-5.08	± 0.28	564
2 (2 m US)	-1.51	± 0.27	564	-13.09	± 0.22	564	-7.87	± 0.31	564
3 (1 m DS)	-0.51	± 0.30	564	-23.54	± 0.46	564	-11.59	± 0.30	564
4 (2 m DS)	-3.14	± 0.31	564	-11.58	± 0.31	564	-4.41	± 0.30	564
5 (3 m DS)	-2.57	± 0.18	564	-11.03	± 0.31	564	-8.44	± 0.25	564
6 (14 m DS)	-5.21	± 0.22	564	-10.76	± 0.31	564	-9.43	± 0.22	564
7 (24 m DS)	-9.29	± 0.18	564	-14.49	± 0.42	564	-13.85	± 0.20	564
8 (34 m DS)	-7.87	± 0.23	564	-13.76	± 0.35	564	-13.72	± 0.34	564
Mean	-4.25	± 0.95	4512	-13.87	± 0.13	4512	-9.30	± 0.11	4512
ANOVA	$F (7, 4504) = 190.62$ p <0.001			$F (7, 4504) = 151.34$ p <0.001			$F (7, 4504) = 167.59$ p <0.001		

Table 7.1 Descriptive statistics for mean daily water table depth by site and by dip-well station along the transect, including ± 1 SE of the mean and sample size (n). The distance in metres (m) of each station from the equivalent ditch area is recorded in either an up-slope (US) or down-slope (DS) direction.

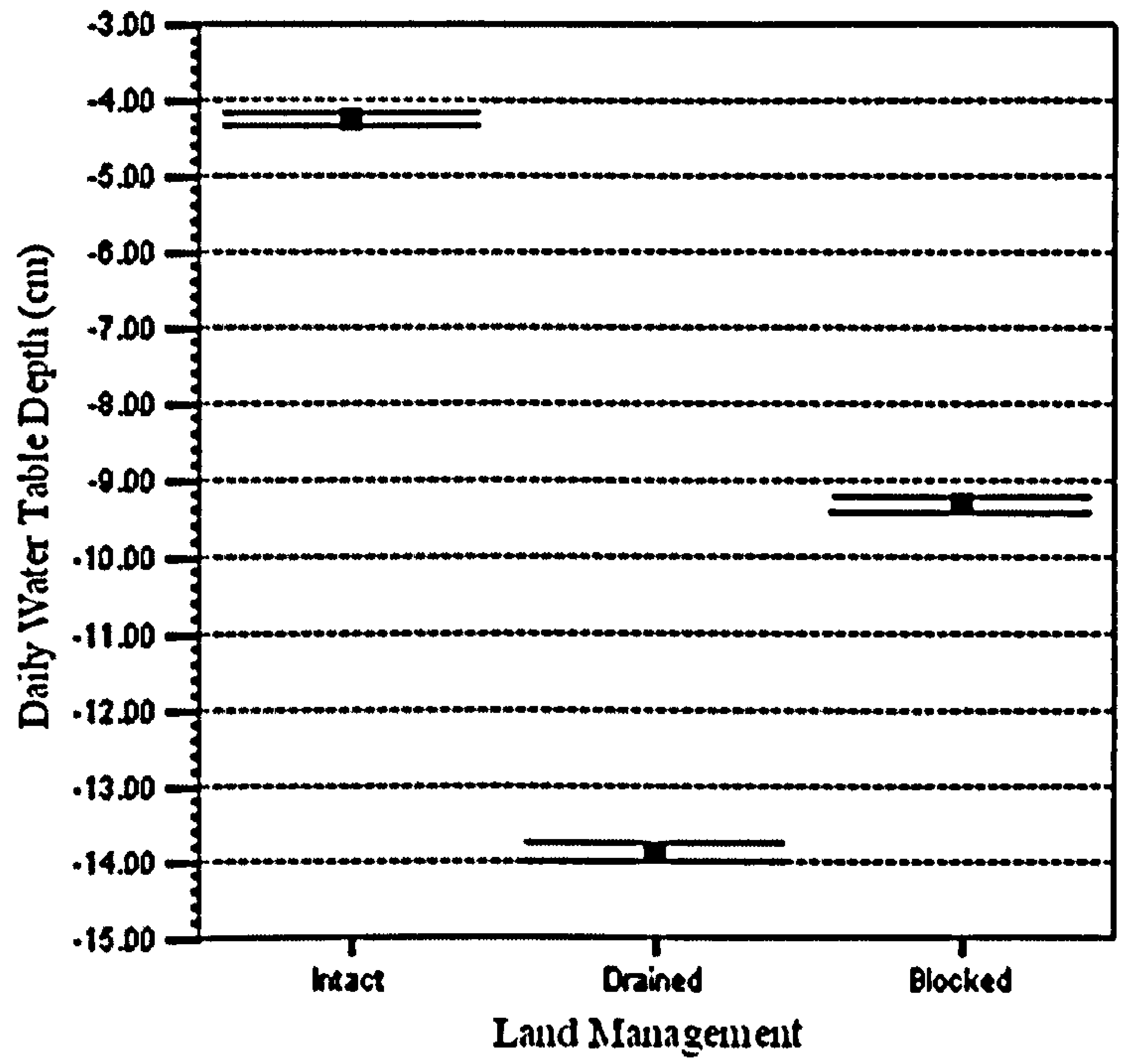


Figure 7.1 Mean daily water table depth for the three treatments, including ± 1 SE of the mean.

The percentage time during the sample period that the mean daily water table was below a certain depth at each site is identified in Figure 7.2. It is clear that the water table at the drained and blocked sites spends a greater proportion of time below the surface compared to the intact site, with the water table at the intact site being located at or below -10 cm for about 20 % of the time, whereas at the drained and blocked sites this was increased to 65 % and 43 % respectively. It can also be seen that for 95 % of the time, the water table at the intact site was above -14.5 cm, whilst at the drained and blocked sites the water table was located at or above -29 cm and -21.5 cm respectively for 95 % of the time. The daily water table depth at each of the eight dip-well stations was also analysed over the sample period. It was found that total surface saturation (i.e. a water table located at or above 0 cm) occurred on at least 107, 17, and 56 days out of 564 for the intact, drained and blocked sites respectively.

ANOVA also identified there were significant (p <0.001) differences in the mean daily water table depth between sample stations located across each site (Table 7.1). Figures 7.3 to 7.5 clearly identify the variance in water table depth across the transect at each of the three sites. The greatest difference in water table depth at the drained site was at the station 1 m down-slope (DS) of the ditch, where the water table was 11.20 cm lower than the mean of the two closest stations situated ≤ 2 m apart. A similar drop in water table depth was also observed at the same station at the blocked site, where the mean depth was 5.45 cm lower compared to the mean of the two closest stations. In addition, the sample stations located nearest the ditch exhibited the greatest range in values in comparison to the locations sampled further away, particularly at the blocked site. Mean values across the intact and blocked sites exhibited similar ranges of 8.78 cm and 9.44 cm respectively, whilst at the drained site the range was larger at 12.78 cm. However, if the station 1 m DS was excluded from analysis for all three sites, the drained site actually exhibits the lowest degree of variability, with a maximum difference between stations of 3.73 cm, whereas at the intact and blocked sites this was greater at 7.78 cm and 9.44 cm respectively.

When the individual dip-well stations were compared between sites, it was found that the drained site had a consistently and significantly ($p < 0.001$) lower mean daily water table depth at each station compared to the intact site (Table 7.1). It also experienced the greatest water table drawdown recorded at any one of the sample stations of -50.44 cm (1 m DS) compared to a maximum of -20.42 cm (2 m DS) at the intact site. In contrast, at the blocked site one of the stations (15 m up-slope) was not found to be significantly different from the corresponding point at the intact site, whilst two stations (14 & 24 m DS) were not found to be significantly different from the corresponding points at the drained site. Furthermore, the maximum drawdown recorded at any one station (-28.24 cm) was far lower compared to the drained site.

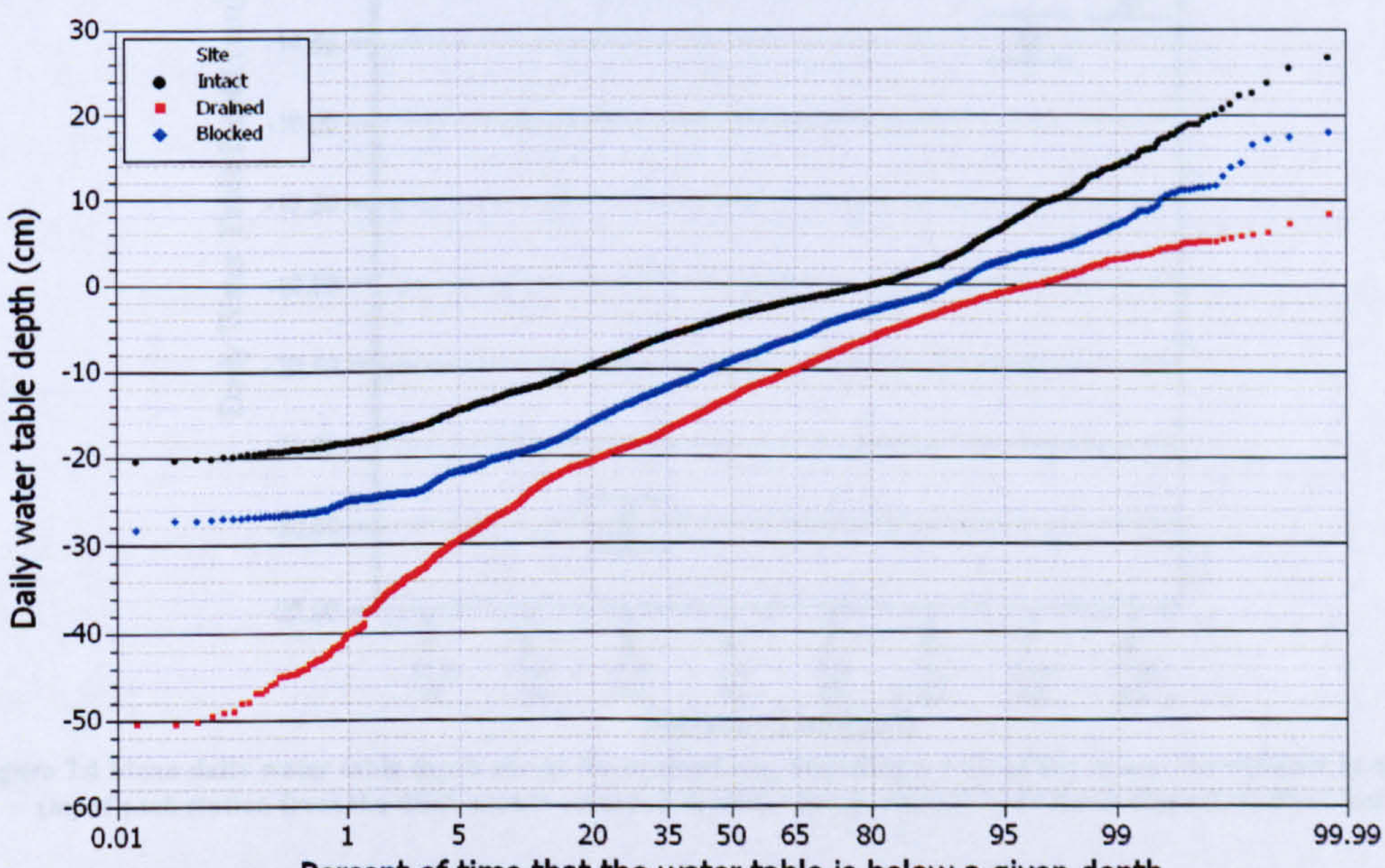


Figure 7.2 Percent of time the water table is below a given depth for each of the three treatments.

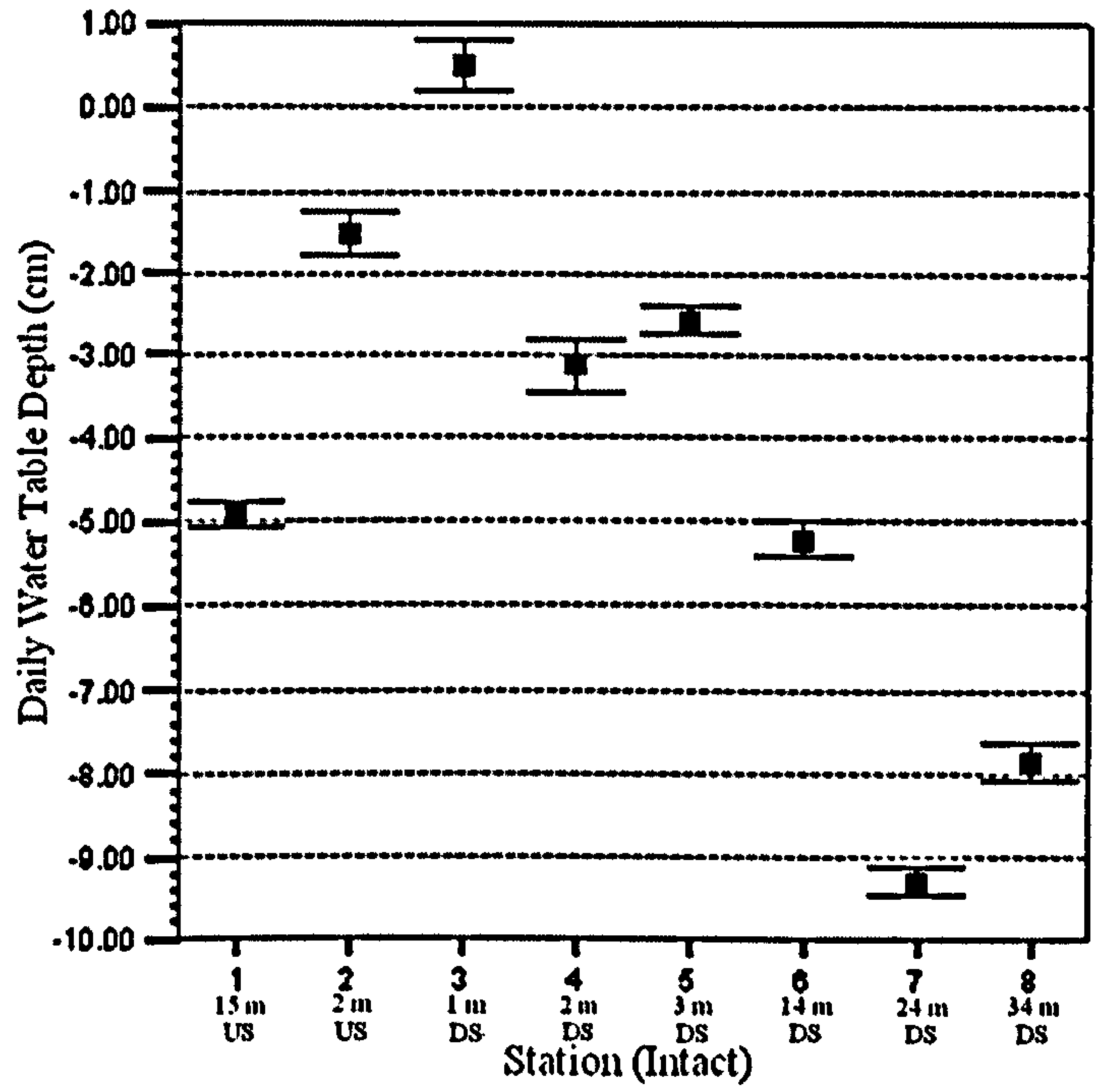


Figure 7.3 Mean daily water table depth across the intact site, including ± 1 SE of the mean. The distance in metres (m) of each station from the equivalent ditch area is recorded in either an up-slope (US) or down-slope (DS) direction.

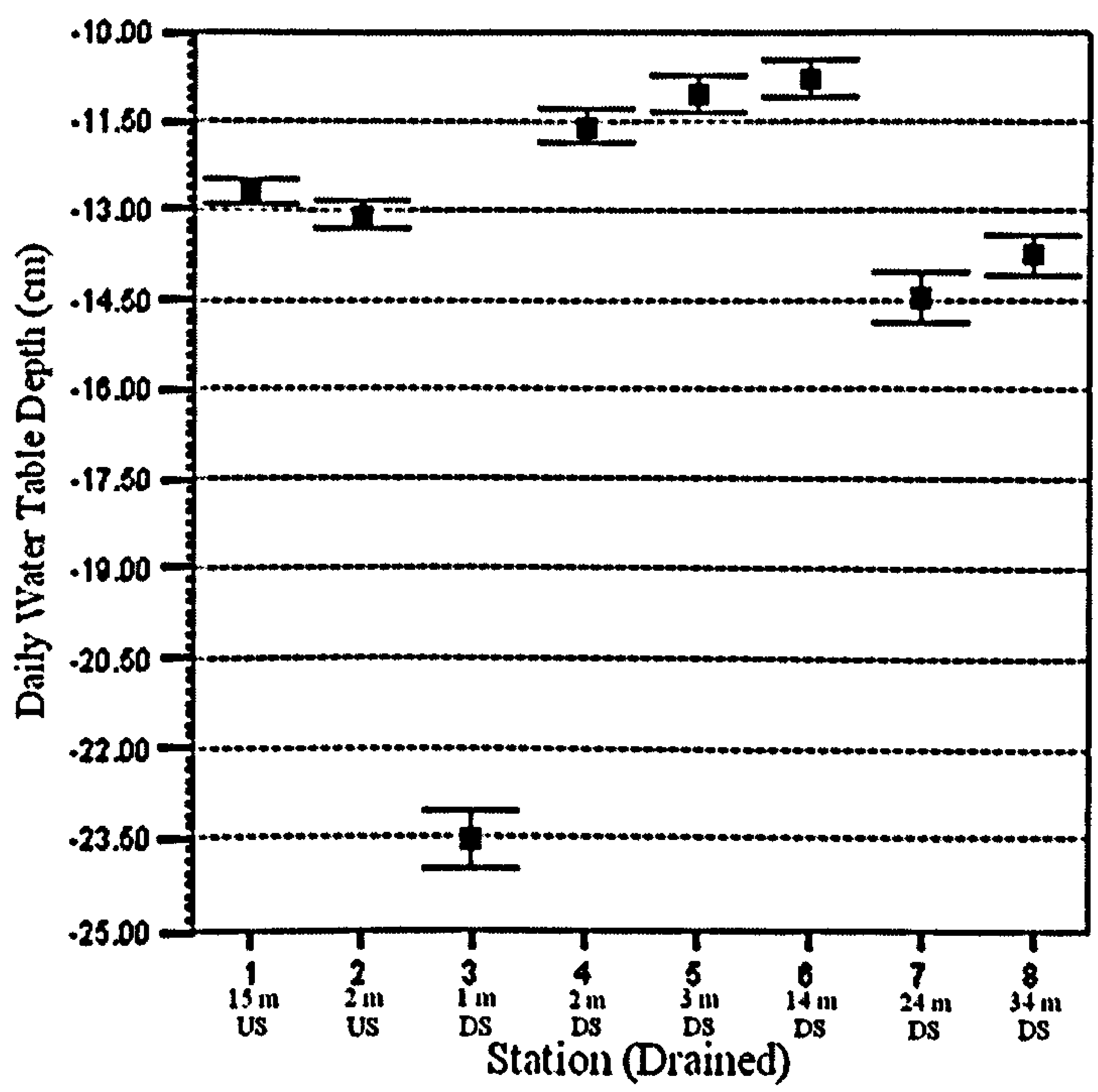


Figure 7.4 Mean daily water table depth across the drained site, including ± 1 SE of the mean. The distance in metres (m) of each station from the ditch area is recorded in either an up-slope (US) or down-slope (DS) direction.

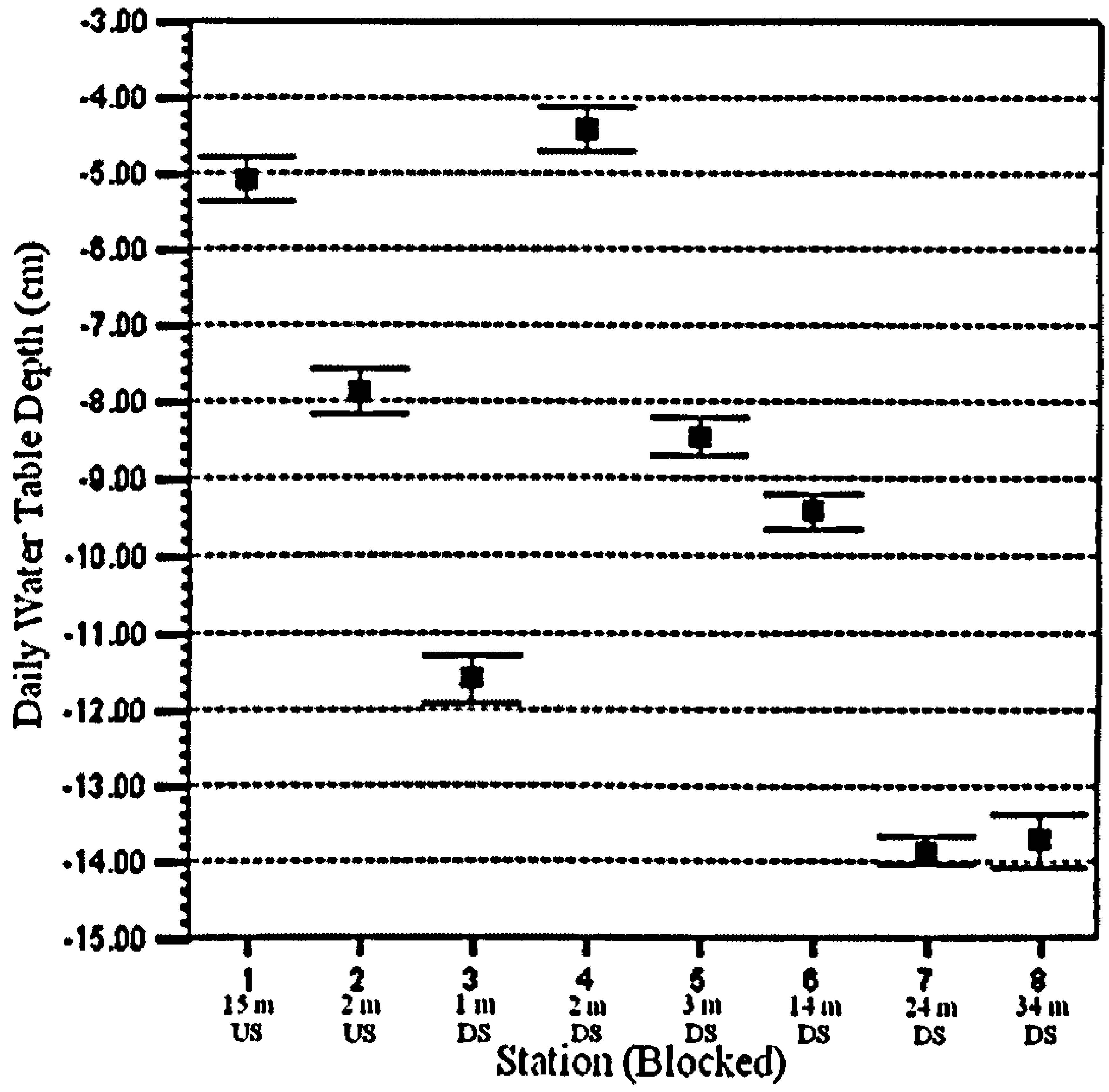


Figure 7. 5 Mean daily water table depth across the blocked site, including ± 1 SE of the mean. The distance in metres (m) of each station from the ditch area is recorded in either an up-slope (US) or down-slope (DS) direction.

The mean daily water table depth for each site was also analysed on a temporal basis in order to identify any seasonal trends in the drained > blocked > intact relationship. It is clear from Figure 7.6 that the water table drawdown observed at the drained site is maintained throughout the sample period, whilst the water table at the blocked site generally remains higher and exhibits a much closer association with the water table at the intact site. Furthermore, it is apparent that the water table at the intact site generally remains within 10 cm of the surface except for short periods during the summer months such as, during July to August 2005 where the water table reached a low of -13 cm (due in part to a reduction in total daily rainfall and an increase in evapotranspiration), and during June to July 2006 where it reached a depth of nearly -14 cm (no rainfall data available). A similar pattern was observed at the drained and blocked site, although the maximum water table depth was far greater during both periods, reaching values of about -27 cm and -20 cm respectively. However, during the period July to August 2005 the drawdown at the drained site was maintained for an extended period of time compared to the intact and blocked sites, with the maximum depth for the site actually recorded in September, after which time mean daily values remained at about a depth of -18 cm until early December 2005, when they rose sharply in response to a period of prolonged and heavy rainfall.

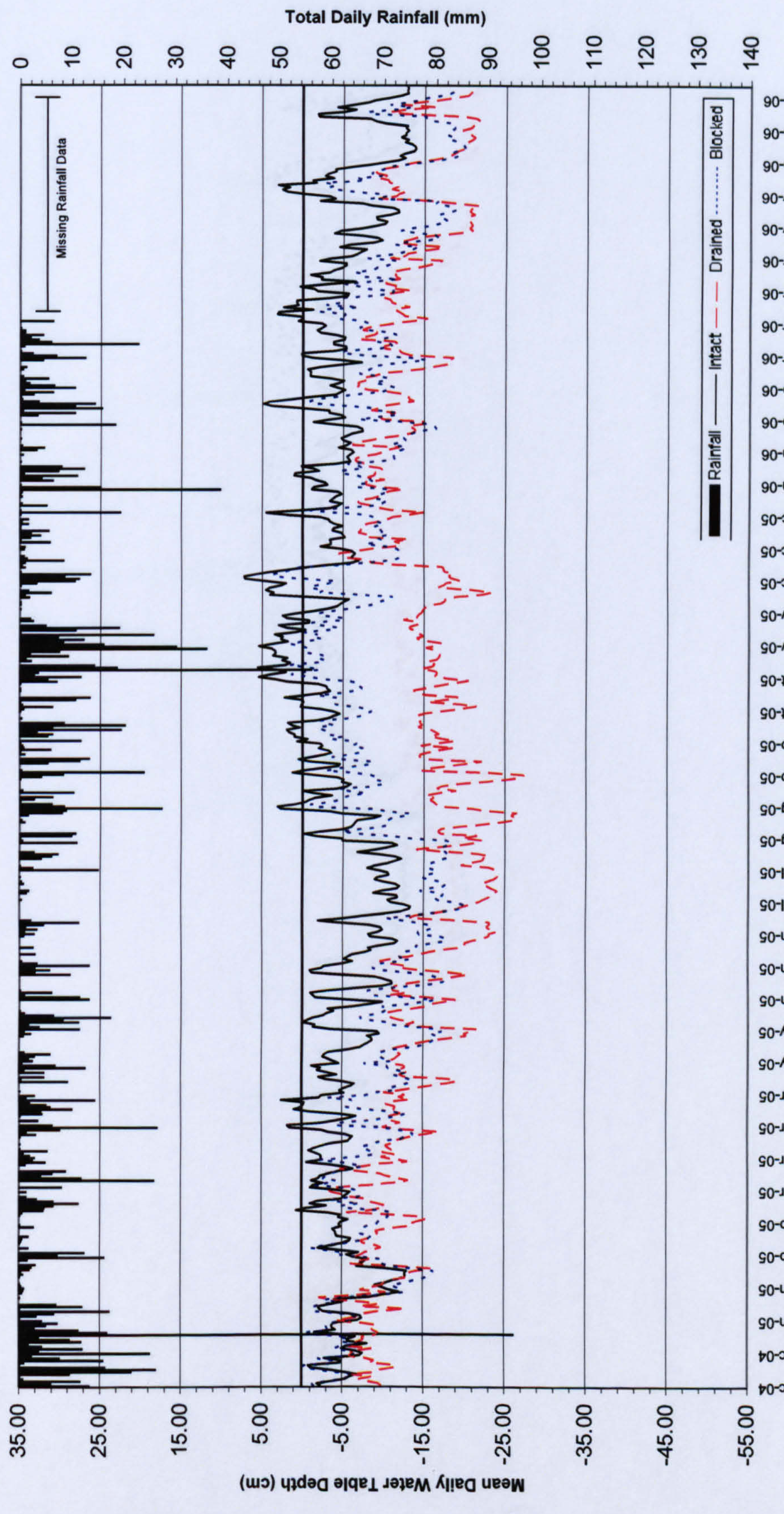


Figure 7.6 Total daily rainfall and mean daily water table depth at each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

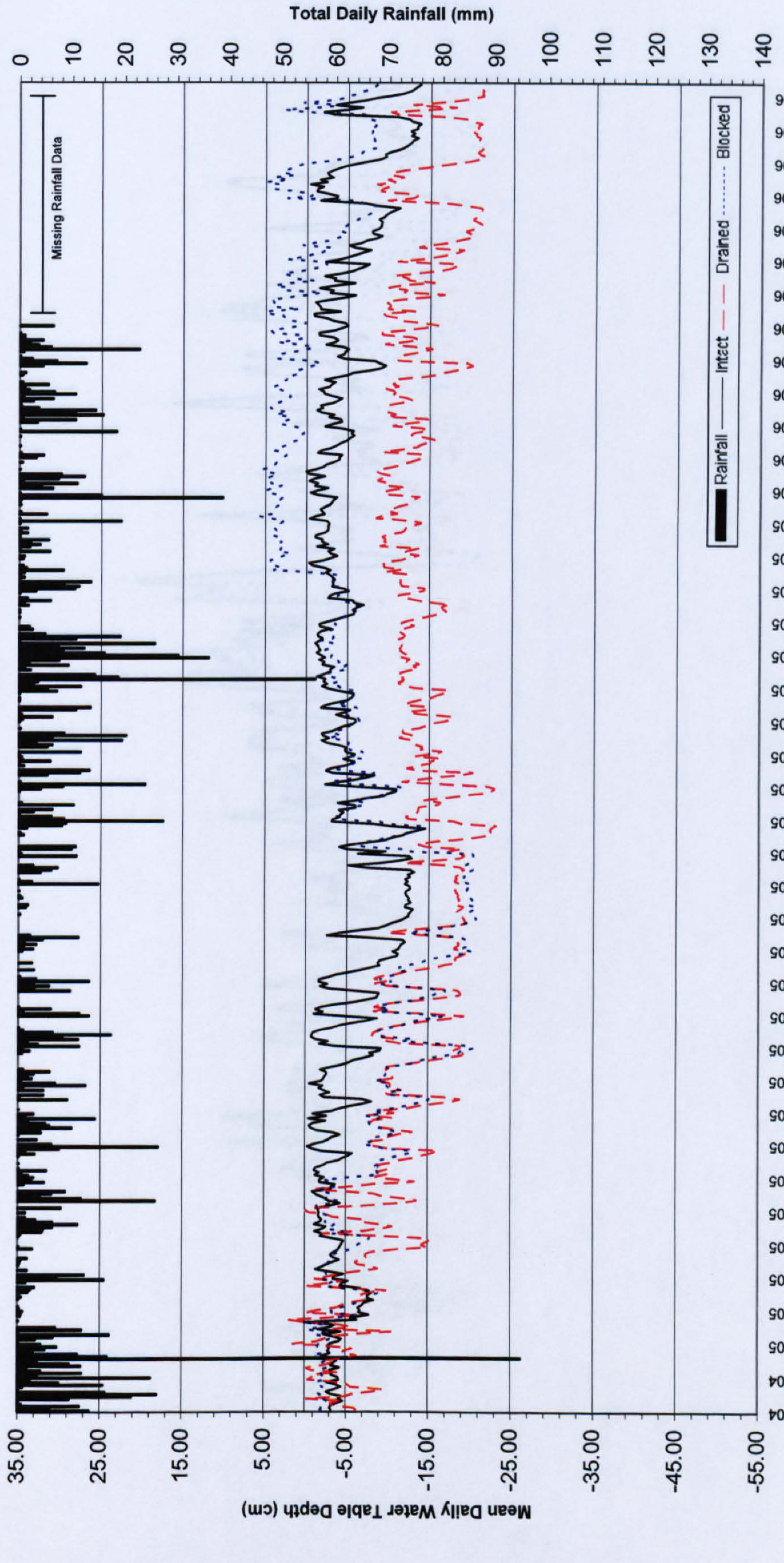


Figure 7.7 Total daily rainfall and mean daily water table depth recorded at 15 m up-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

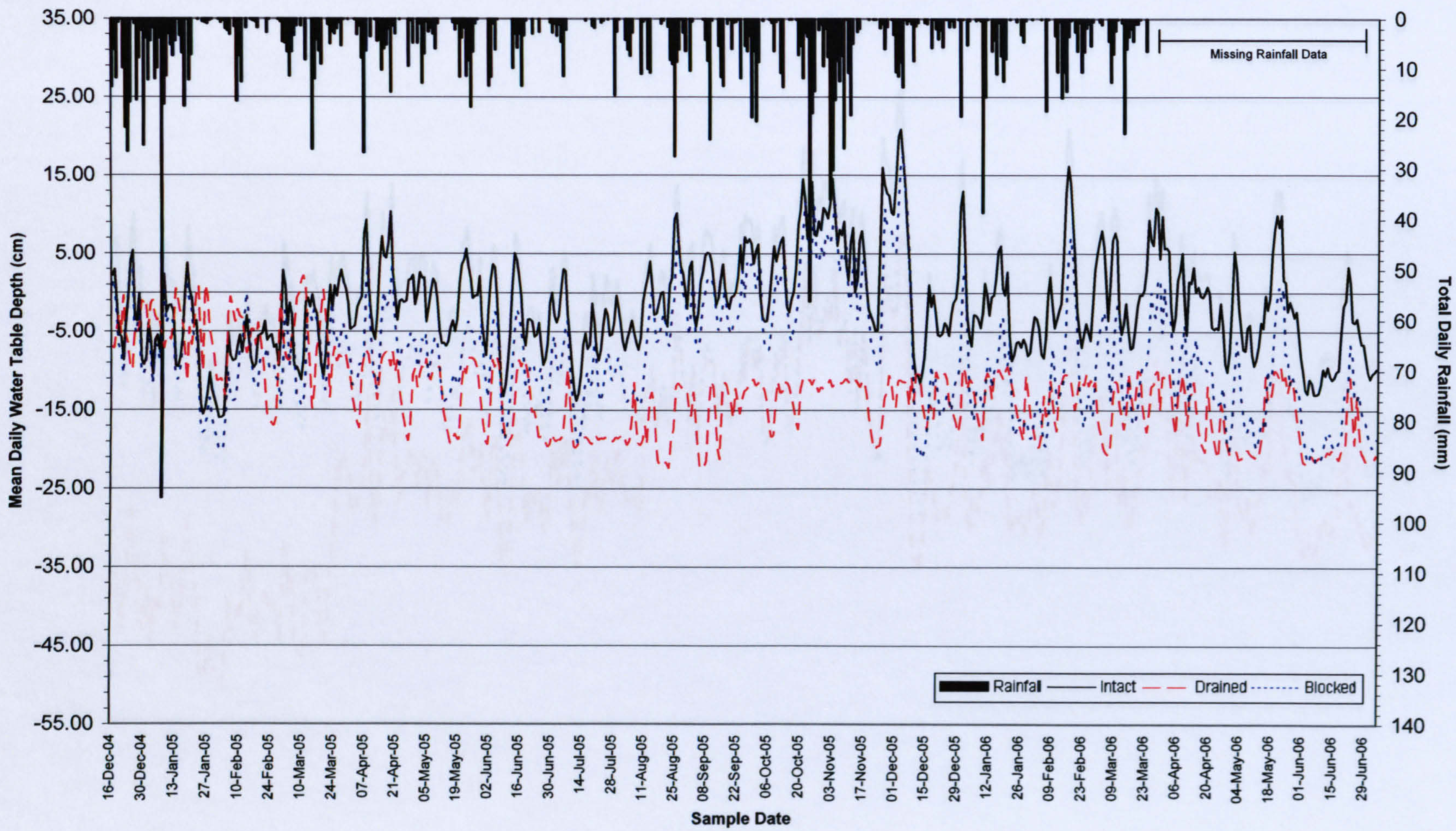


Figure 7.8 Total daily rainfall and mean daily water table depth recorded at 2 m up-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

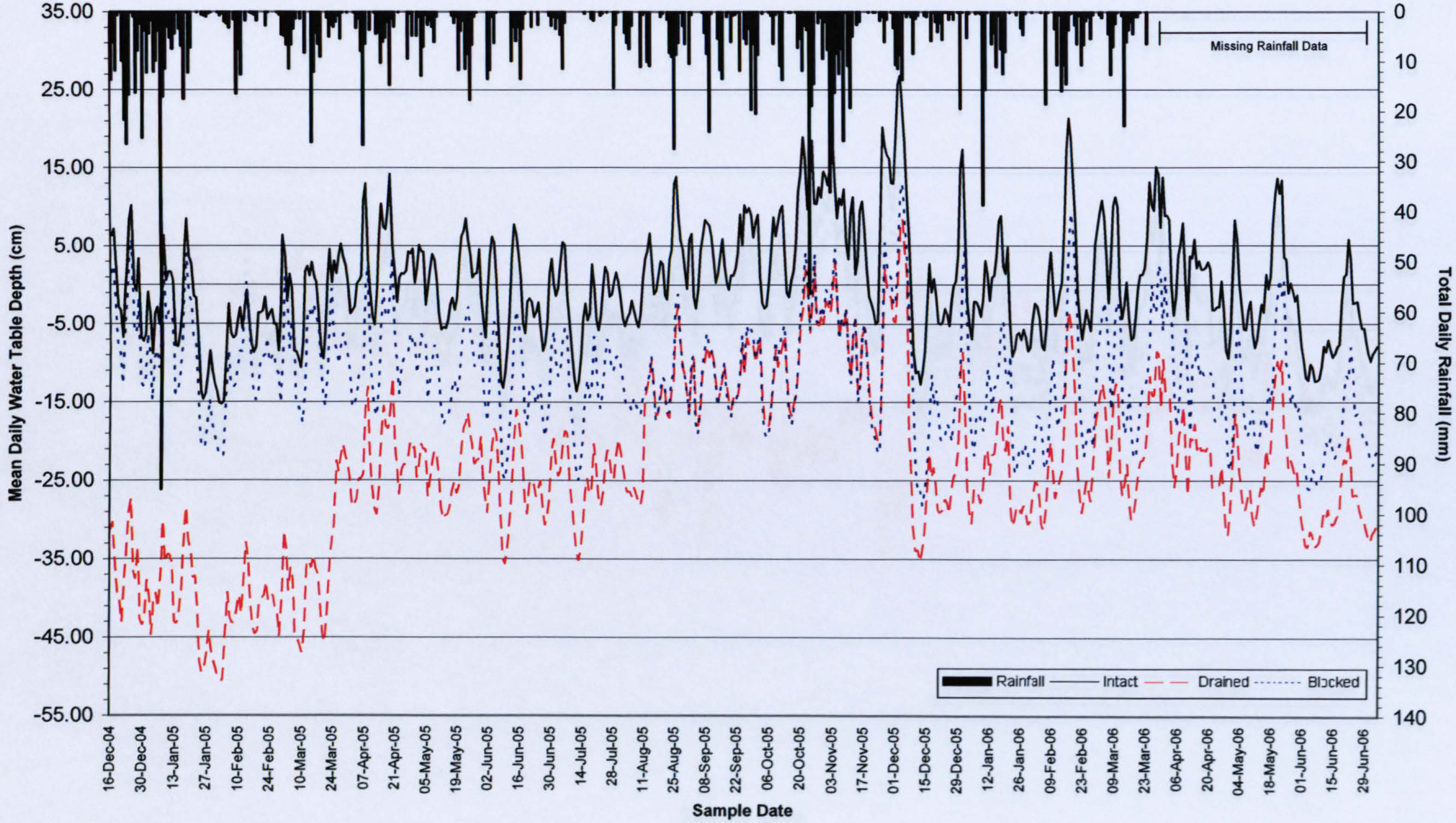


Figure 7.9 Total daily rainfall and mean daily water table depth recorded at 1 m down-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

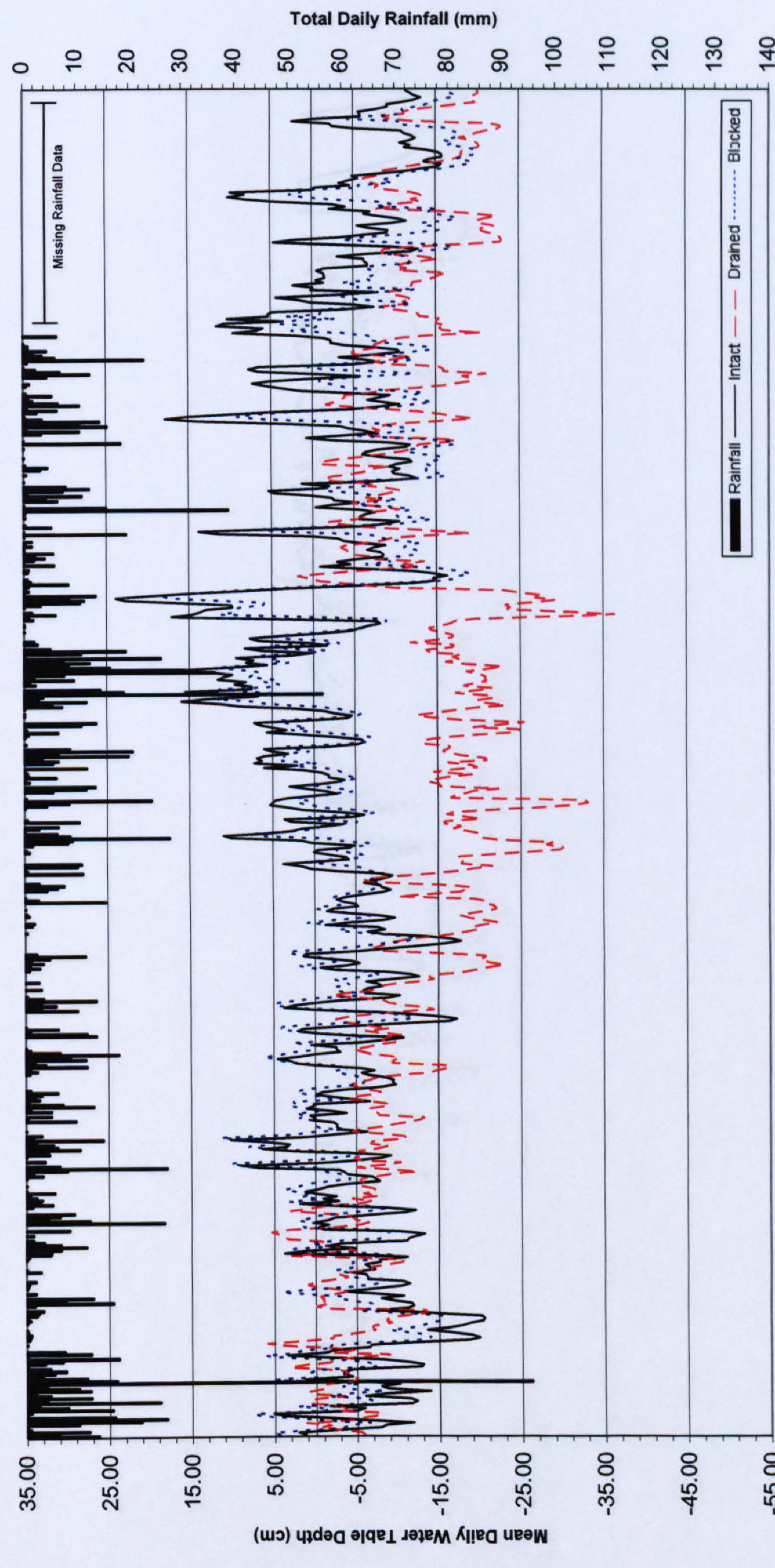


Figure 7.10 Total daily rainfall and mean daily water table depth recorded at 2 m down-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

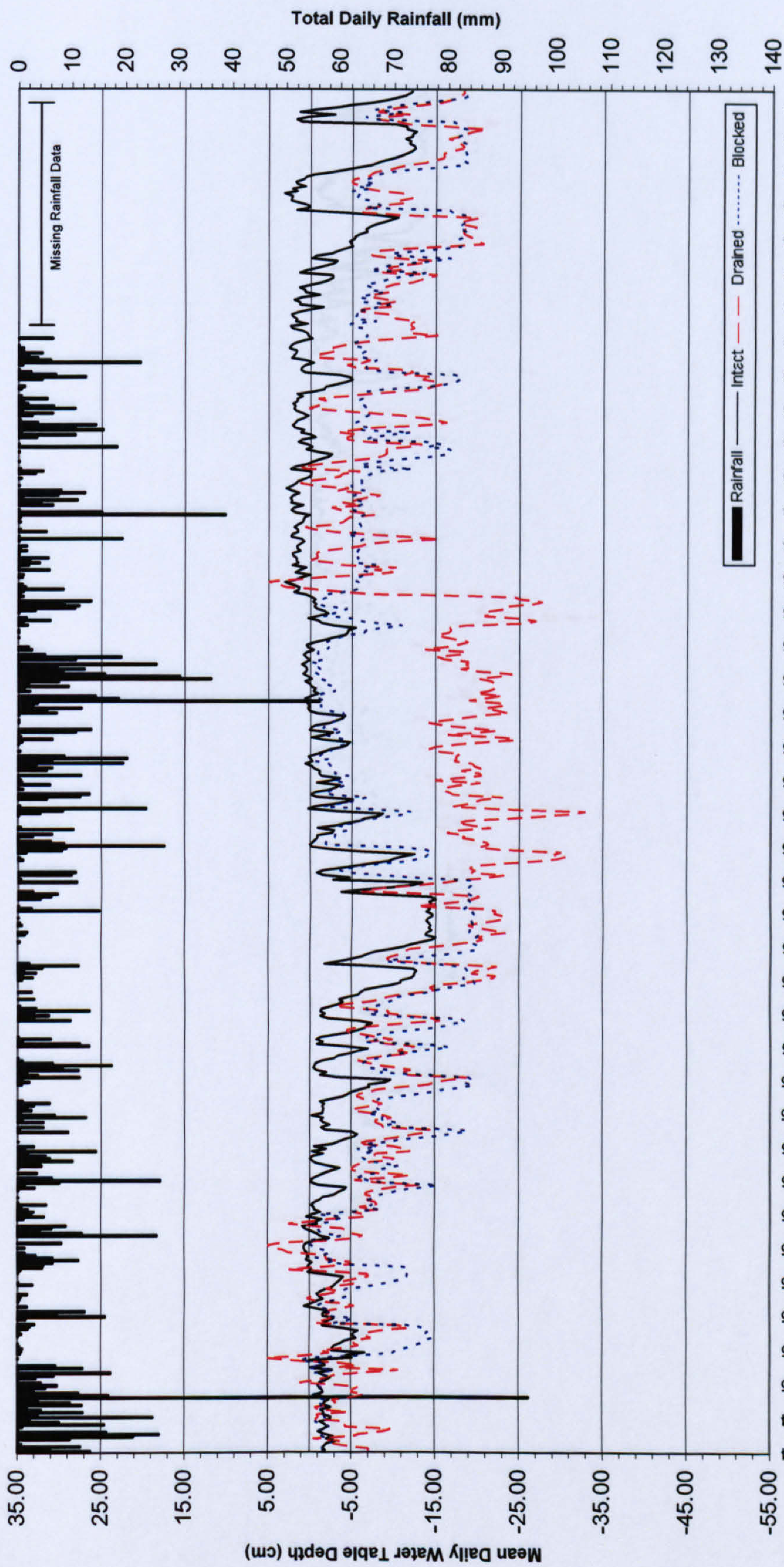


Figure 7.11 Total daily rainfall and mean daily water table depth recorded at 3 m down-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

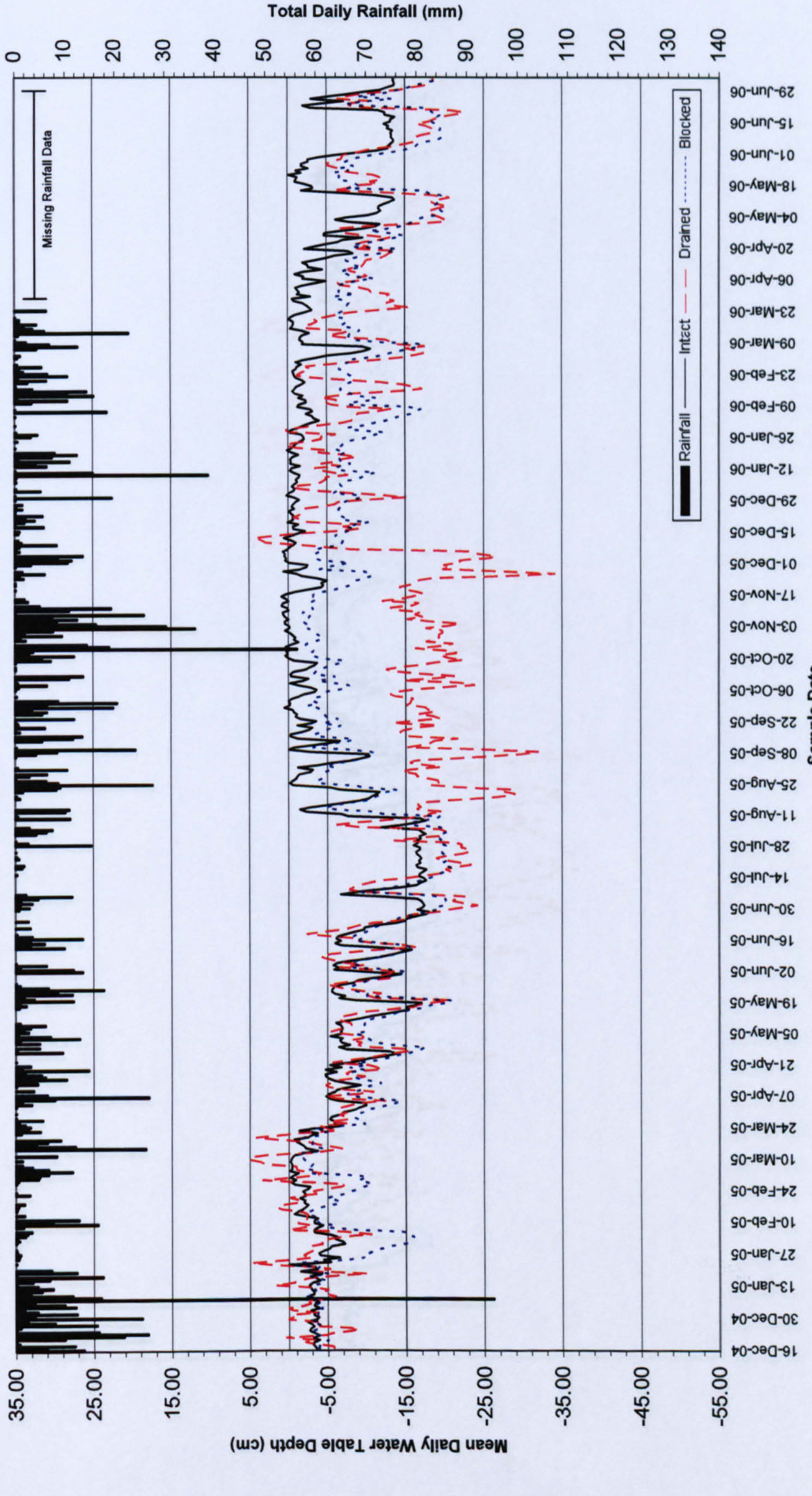


Figure 7.12 Total daily rainfall and mean daily water table depth recorded at 14 m down-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

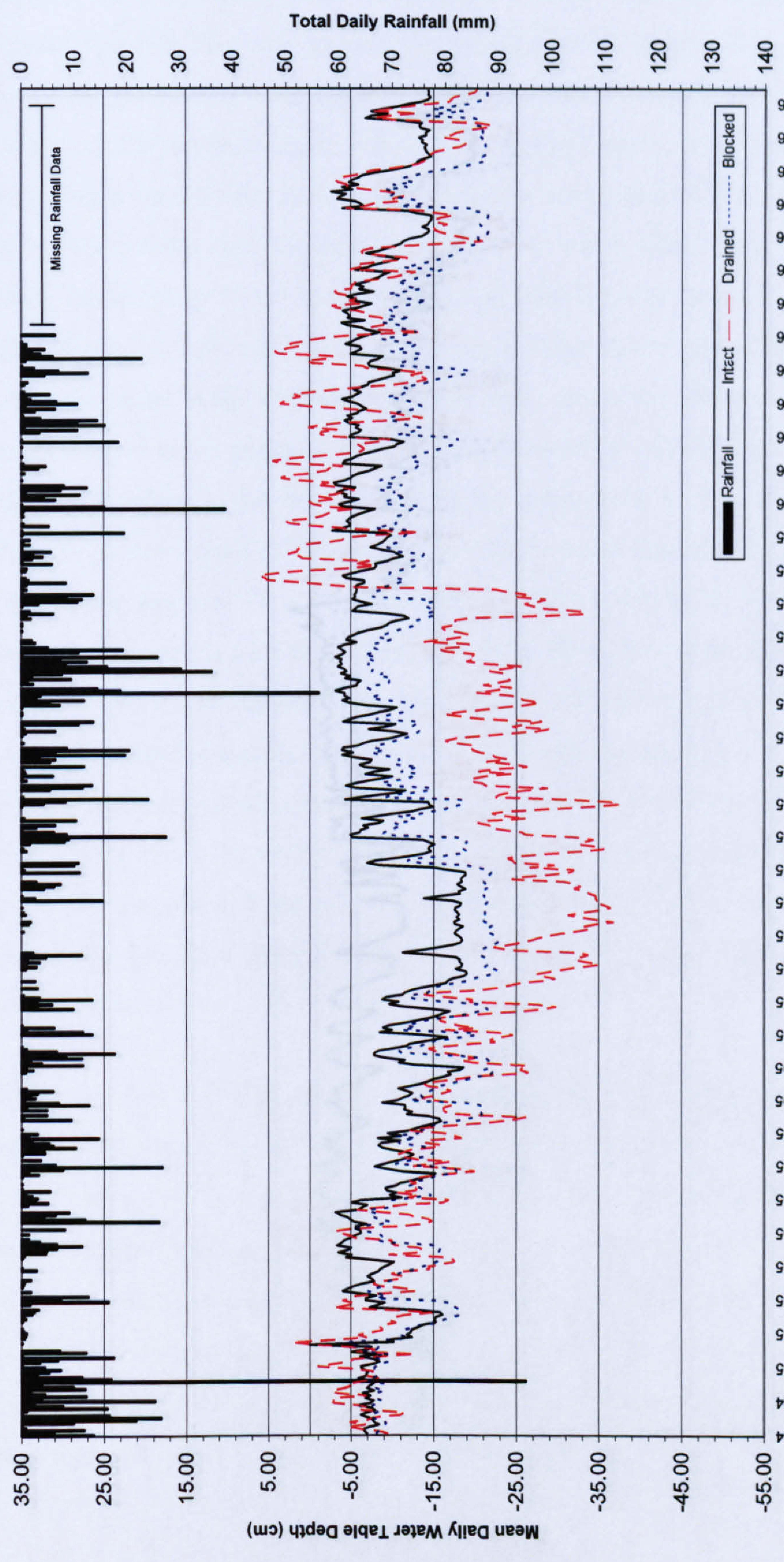


Figure 7.13 Total daily rainfall and mean daily water table depth recorded at 24 m down-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

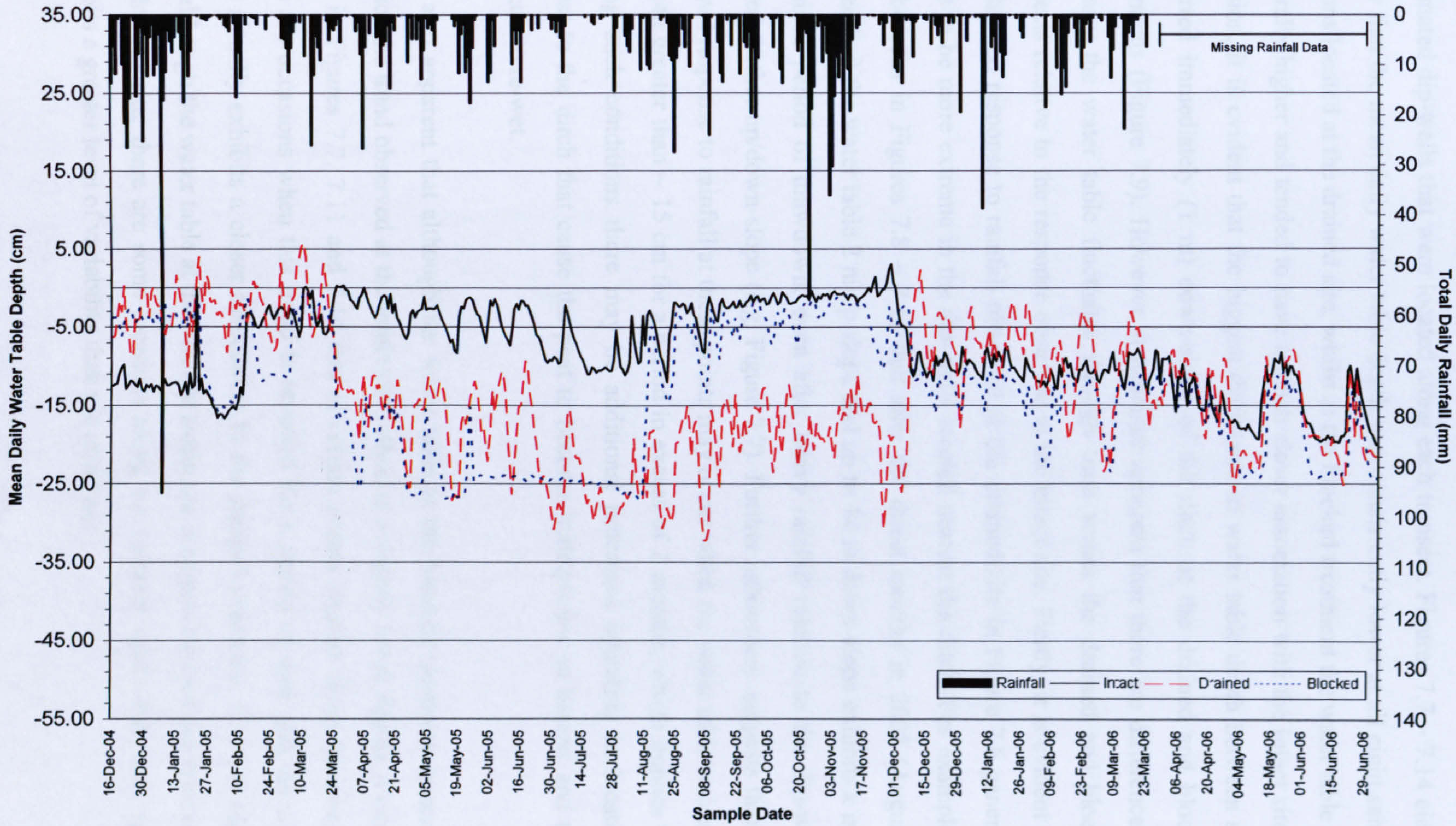


Figure 7.14 Total daily rainfall and mean daily water table depth recorded at 34 m down-slope from the ditch (or equivalent area) for each treatment across the sample period December 2004 to July 2006. Values above 0 cm for the water table indicate periods of total saturation and therefore surface ponding.

Temporal trends in the water table were also assessed on a spatial scale for each site by plotting the mean daily water table depth through time for each of the eight automated dip-wells that were located along each transect. Figures 7.7 – 7.14 clearly show that the mean daily water table depth was consistently lower at all eight sample stations located at the drained site, whilst at the blocked treatment the water table was generally higher and tended to have a much closer association with the intact site. In addition, it is evident that the biggest difference in water table depth between sites occurred immediately (1 m) down-slope of the ditch at the drained and blocked treatments (Figure 7.9). However, it becomes apparent that there are differences in the way the water table fluctuates through time across the drained and blocked transects relative to the response observed at the intact site. Firstly, it is evident that the delayed response to rainfall observed at the drained site in Figure 7.6 generally tends to be more extreme in the dip-wells located nearest the ditch. For example, it can be seen in Figures 7.8 – 7.12 that after the driest months in 2005 (August – November) the water table 2 m up-slope and up to 14 m down-slope exhibits a more sustained period of drawdown, even after heavy rainfall relative to the dip-wells located further up/down-slope (e.g. Figure 7.7). Further assessment suggests that the delayed response to rainfall at these points may occur when the water table resides at a depth greater than ~ 15 cm for a period in excess of 2 months, which implies that during such conditions there may be additional processes operating in locations closest to the ditch that cause the peat to become hydrophobic in nature, and thus difficult to re-wet.

It is also apparent that although the water table at the blocked treatment generally mimics the trend observed at the intact site (albeit at a slightly lower depth), it can be seen in Figures 7.7, 7.11 and 7.14 that at certain points located along the transect there are occasions when this trend is reversed for a period of time and the water table actually exhibits a closer association to the drained treatment. Thus, it seems that although the water table at the blocked treatment is somewhat restored relative to the drained site, there are some locations along the transect where the water table exhibits a greater level of variability than the intact site.

7.3.2. OVERLAND FLOW

ANOVA identified there to be a significant (p <0.001) amount of variation in the percentage occurrence of OLF between the three sites (Figure 7.15), with independent t-tests revealing that the mean occurrence of OLF at the intact site of 93 % was significantly greater than that of the drained (p <0.001) and blocked sites (p = 0.02), where surface runoff was only recorded for 61 % and 84 % of monthly visits, respectively. However, in contrast the percentage occurrence of OLF at the blocked site was found to be significantly (p <0.001) higher than that of the drained site. In addition, the range of values recorded across the drained (44 % to 75 %) and blocked sites (56 % to 100 %) was found to be nearly double that observed across the intact transect (80 % to 100 %). This indicates that there is a greater level of variability in the level of surface saturation at the disturbed sites, which corresponds well with the mean water table depth relationship identified in Section 7.3.1. However, it also suggests that a greater proportion of the runoff produced at the drained and blocked sites is likely to occur as subsurface flow, and indicates there may have also been changes to the structural and infiltration properties of the peat.

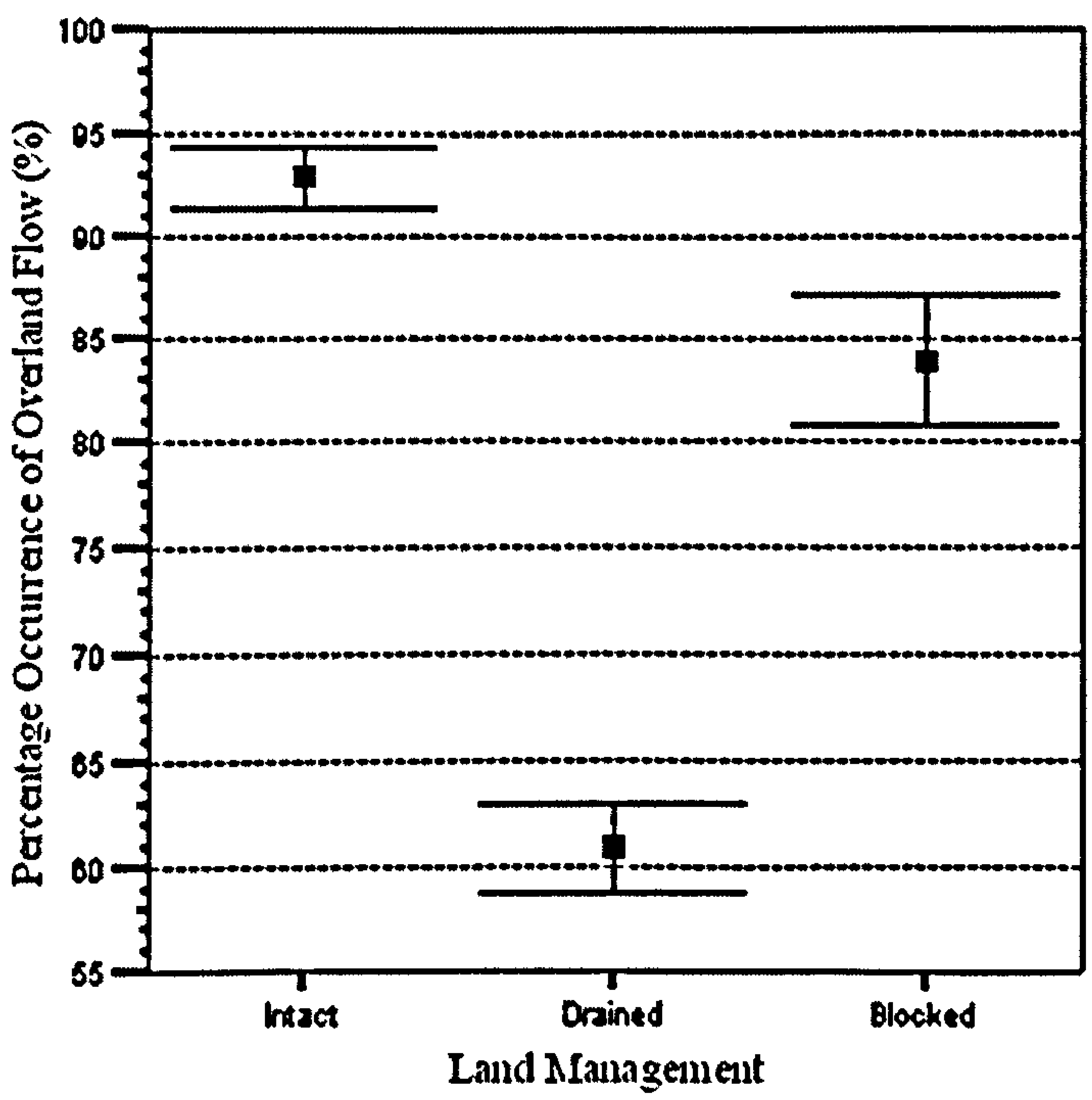


Figure 7.15 Mean percentage occurrence of OLF at each of the three treatments, including ± 1 SE of the mean.

7.3.3. MACROPOROSITY AND HYDRAULIC CONDUCTIVITY

Assessment of the infiltration properties of the blanket peat soils at Oughtershaw identified that subsurface runoff was dominated by a high proportion of macropore flow, with all three sites exhibiting values >60 %. However, ANOVA identified there to be significant ($p = 0.001$) differences between the three treatments, indicating that the water table disturbance associated with the varying land management techniques has resulted in changes to the structural characteristics of the peat soil (Table 7.2). Independent t-tests revealed that the contribution to throughflow from macropores at the intact site (74 %) was significantly ($p < 0.002$) higher compared to both the drained (66 %) and blocked sites (60 %), whilst although the level of macroporosity at the drained site was higher than that observed at the blocked site, this was not found to be significant at the 95 % confidence level ($p = 0.068$). (Figure 7.16).

Rates of surface hydraulic conductivity appeared to be consistent with those previously reported for blanket peat soils, with mean values recorded at the intact, drained and blocked sites being 1.07×10^{-3} cm s^{-1}, 9.87×10^{-4} cm s^{-1}, and 1.56×10^{-3} cm s^{-1} respectively. The variance in surface hydraulic conductivity observed across the three sites appeared to be relatively high, with rates varying by up to an order of magnitude, with the intact site exhibiting the largest variability with rates ranging from 4.97×10^{-4} cm s^{-1} to 1.50×10^{-3} cm s^{-1}, whilst the drained and blocked sites exhibited slightly smaller ranges of 6.17×10^{-4} cm s^{-1} to 1.51×10^{-3} cm s^{-1}, and 9.80×10^{-4} cm s^{-1} to 2.44×10^{-3} cm s^{-1} respectively. Nonetheless, as Figure 7.17 shows ANOVA identified significant ($p = 0.001$) differences in the mean rate of hydraulic conductivity between the three sites, which indicates that in addition to the structural alterations identified above, there have also been changes to the infiltration characteristics of the peat. However, further analysis revealed a rather unexpected relationship whereby even though the blocked soil had the lowest proportion of macropore flow, it actually exhibited a significantly higher rate of hydraulic conductivity compared to both the intact ($p = 0.008$) and drained ($p < 0.001$) sites. In addition, whilst the intact site exhibited a far higher degree of macroporosity compared to the drained site, no significant ($p = 0.5$) difference in the mean hydraulic conductivity rate was identified between the two treatments.

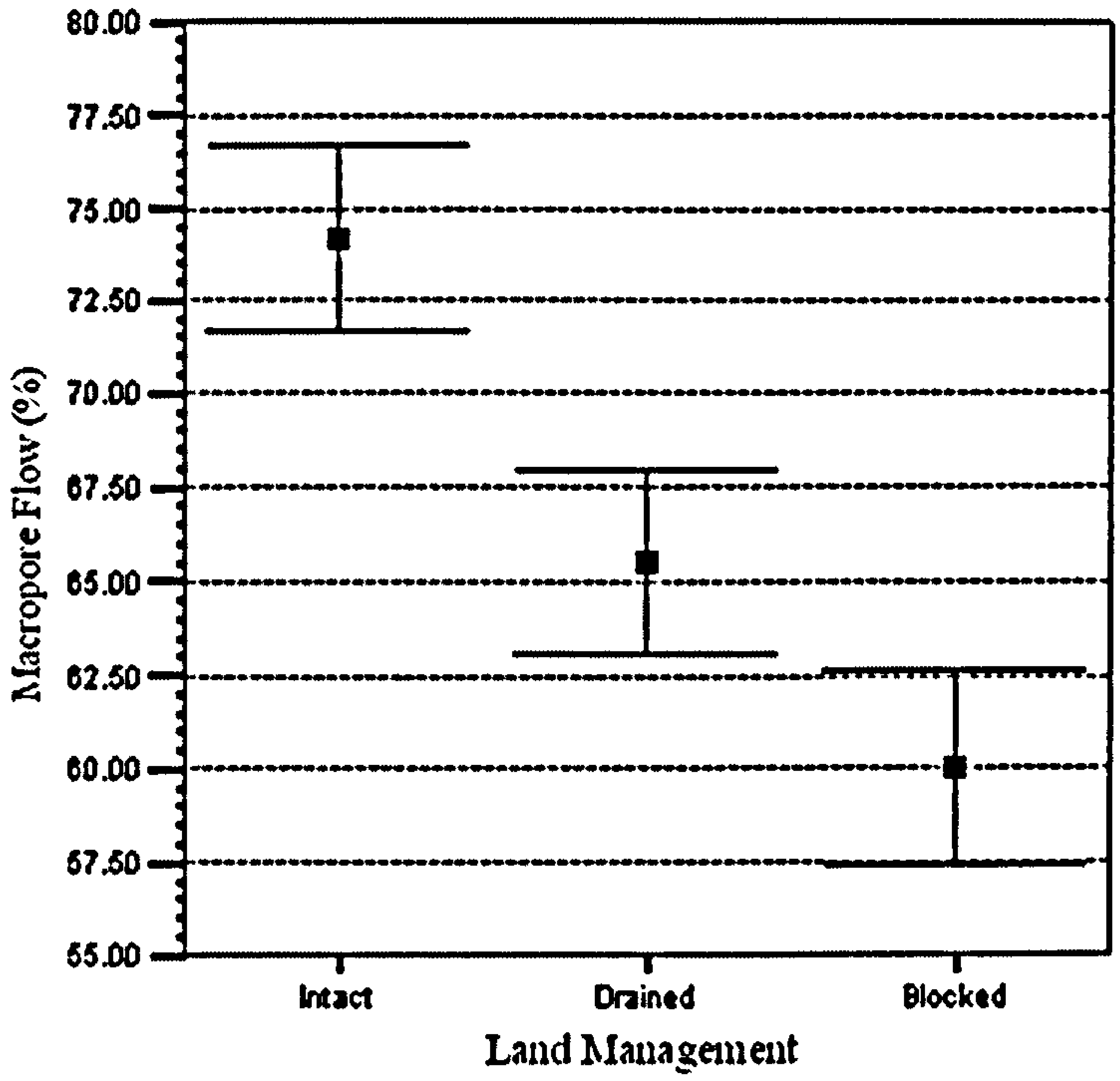


Figure 7.16 Mean percentage macropore flow for each site, including ± 1 SE of the mean.

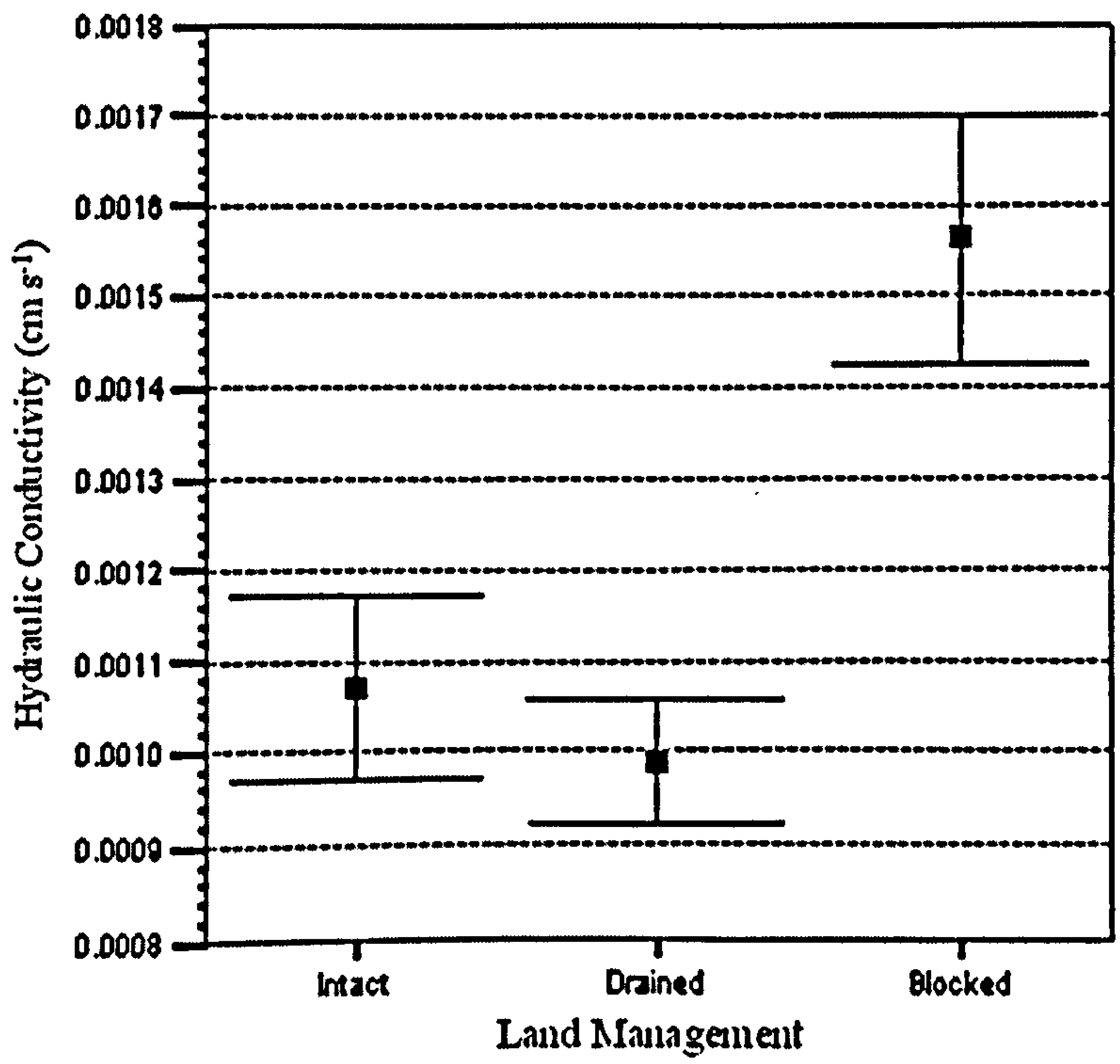


Figure 7.17 Mean rate of hydraulic conductivity for each site, including ± 1 SE of the mean.

7.3.4. BULK DENSITY

When the level of bulk density was compared amongst the three land managements, it was found that the soil at the drained site had a greater bulk density (0.112 g cm^{-3}) than the intact site (0.108 g cm^{-3}), whilst both sites had higher mean values compared to the blocked treatment (0.103 g cm^{-3}). However, as seen in Figure 7.18 no significant (p = 0.605) differences in soil bulk density were identified between the three treatments. Data was also analysed by soil depth within each of the three sites, with Figures 7.19 to 7.21 and Table 7.3 identifying a trend of increasing bulk density with soil depth, particularly at the intact and blocked sites. At the intact site, in addition to a general increase in bulk density with depth there appears to be a distinct elevation in values between 10 and 20 cm depth, whilst at the blocked site there are two stepped increases in bulk density with depth, with values rising sharply between 5 and 10 cm, and between 20 and 40 cm. In contrast, at the drained site although there appears to be a slight increase in bulk density with depth, there are no obvious differences between depths with the soil profile generally appearing more homogenous in comparison to the intact and blocked sites. Further assessment with ANOVA identified that although there was a significant (p = 0.032) increase in bulk density with soil depth at the blocked site, no significant differences between depths were observed at either the intact (p = 0.454) or drained (p = 0.885) treatments. In addition, when values from corresponding soil depths were compared between sites, significant differences were only identified at 5 cm where the bulk density at the blocked treatment was found to be lower (p = 0.034) than that of the drained site.

Bulk Density ($g\ cm^{-3}$)	Treatment								
	Intact			Drained			Blocked		
	Mean	St Error	n	Mean	St Error	n	Mean	St Error	n
5 cm	0.095	± 0.015	6	0.108	± 0.015	6	0.075	± 0.007	6
10 cm	0.099	± 0.016	6	0.109	± 0.007	6	0.102	± 0.011	6
20 cm	0.116	± 0.009	6	0.114	± 0.010	6	0.103	± 0.014	6
40 cm	0.121	± 0.013	6	0.118	± 0.009	6	0.133	± 0.017	6
Mean	**0.108**	**± 0.007**	**24**	**0.112**	**± 0.005**	**24**	**0.103**	**± 0.007**	**24**
ANOVA	**$F_{(3, 20)}$ = 0.909, p = 0.454**			**$F_{(3, 20)}$ = 0.215, p = 0.885**			**$F_{(3, 20)}$ = 3.578, p = 0.032**		

Table 7.2 Descriptive statistics for mean bulk density by site and by soil depth for the three treatments, including ± 1 SE of the mean and sample size (n).

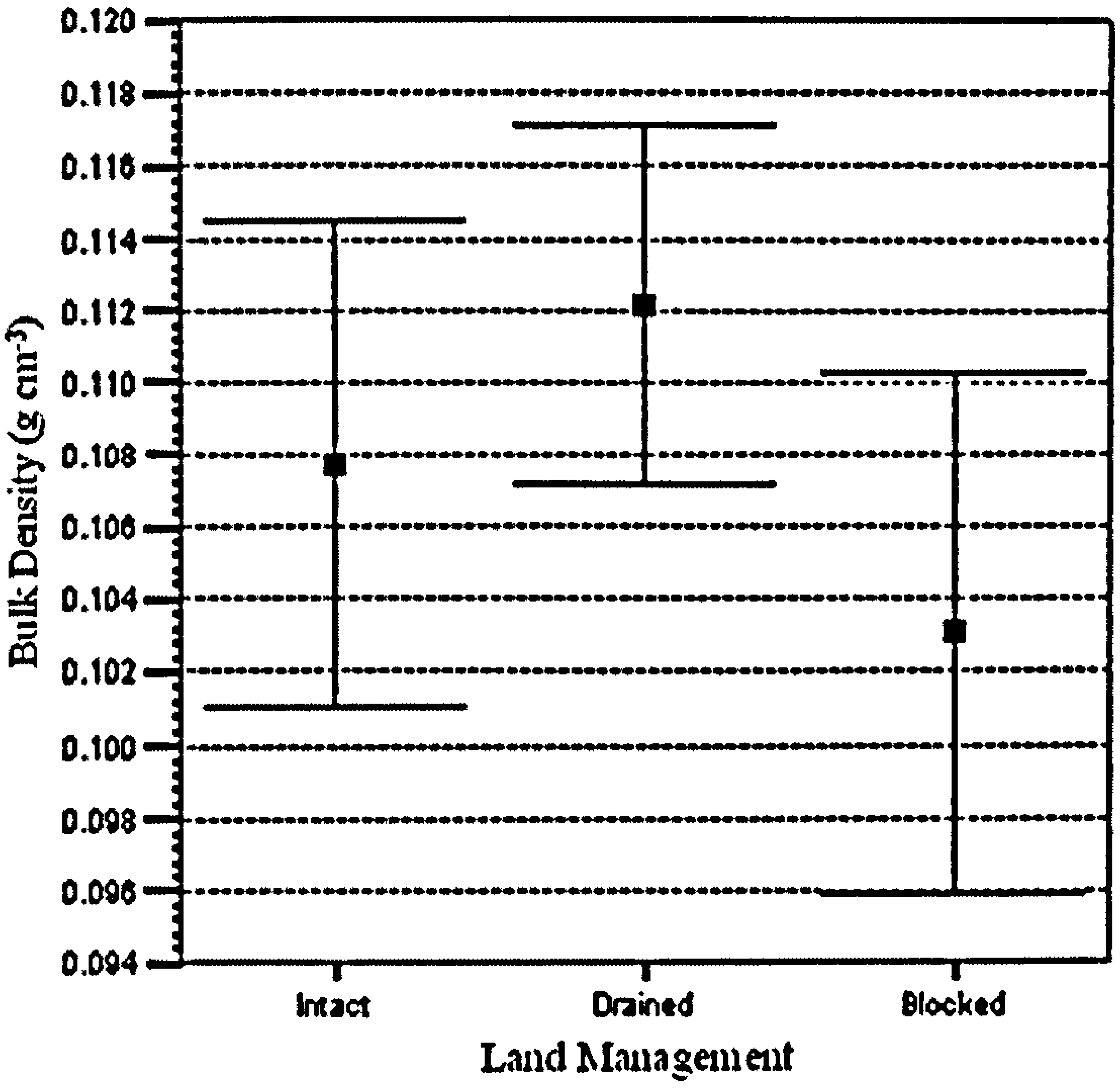


Figure 7.18 Mean bulk density values for each site, including ± 1 SE of the mean.

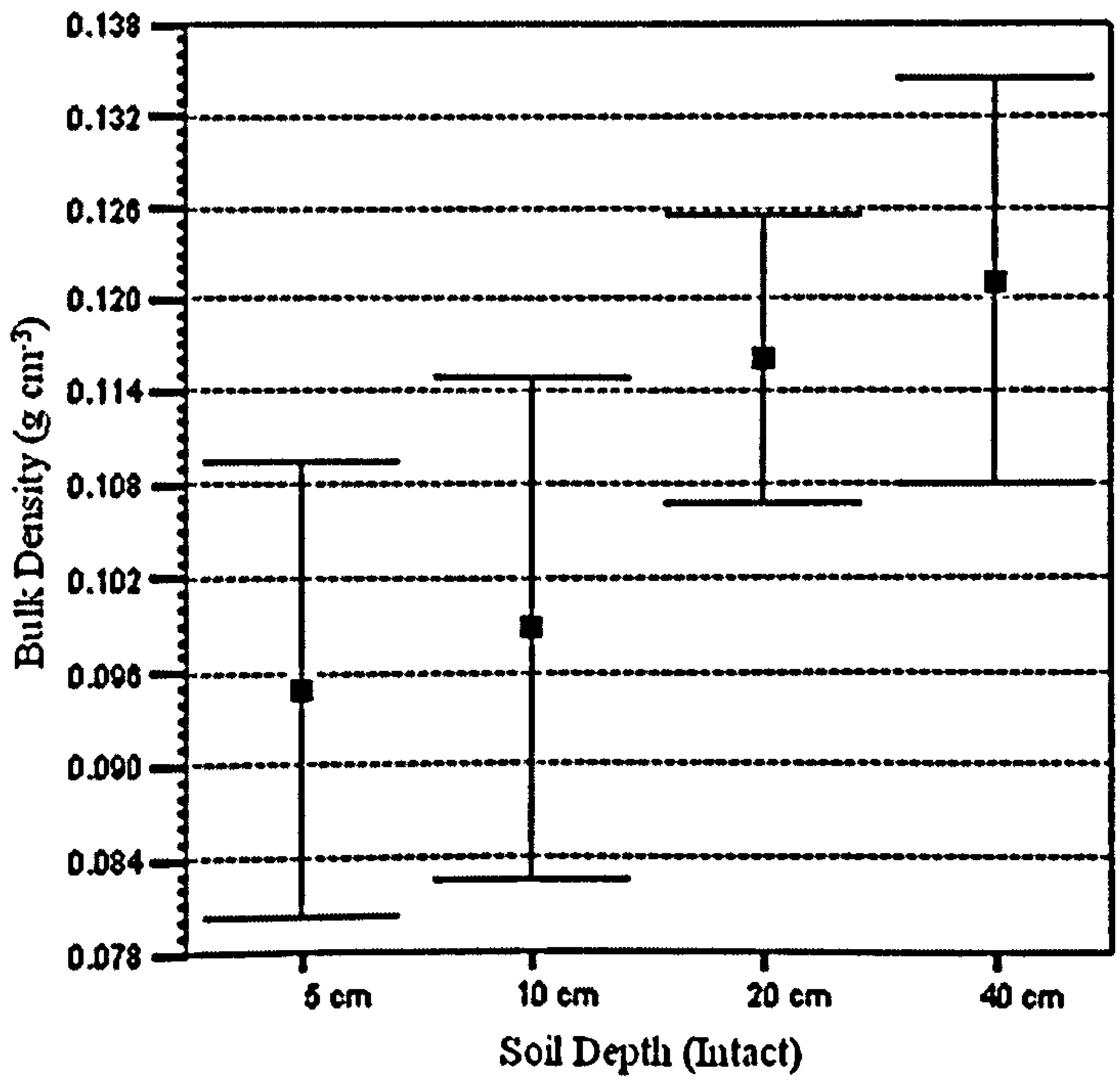


Figure 7.19 Mean bulk density values by soil depth for the intact site, including ± 1 SE of the mean.

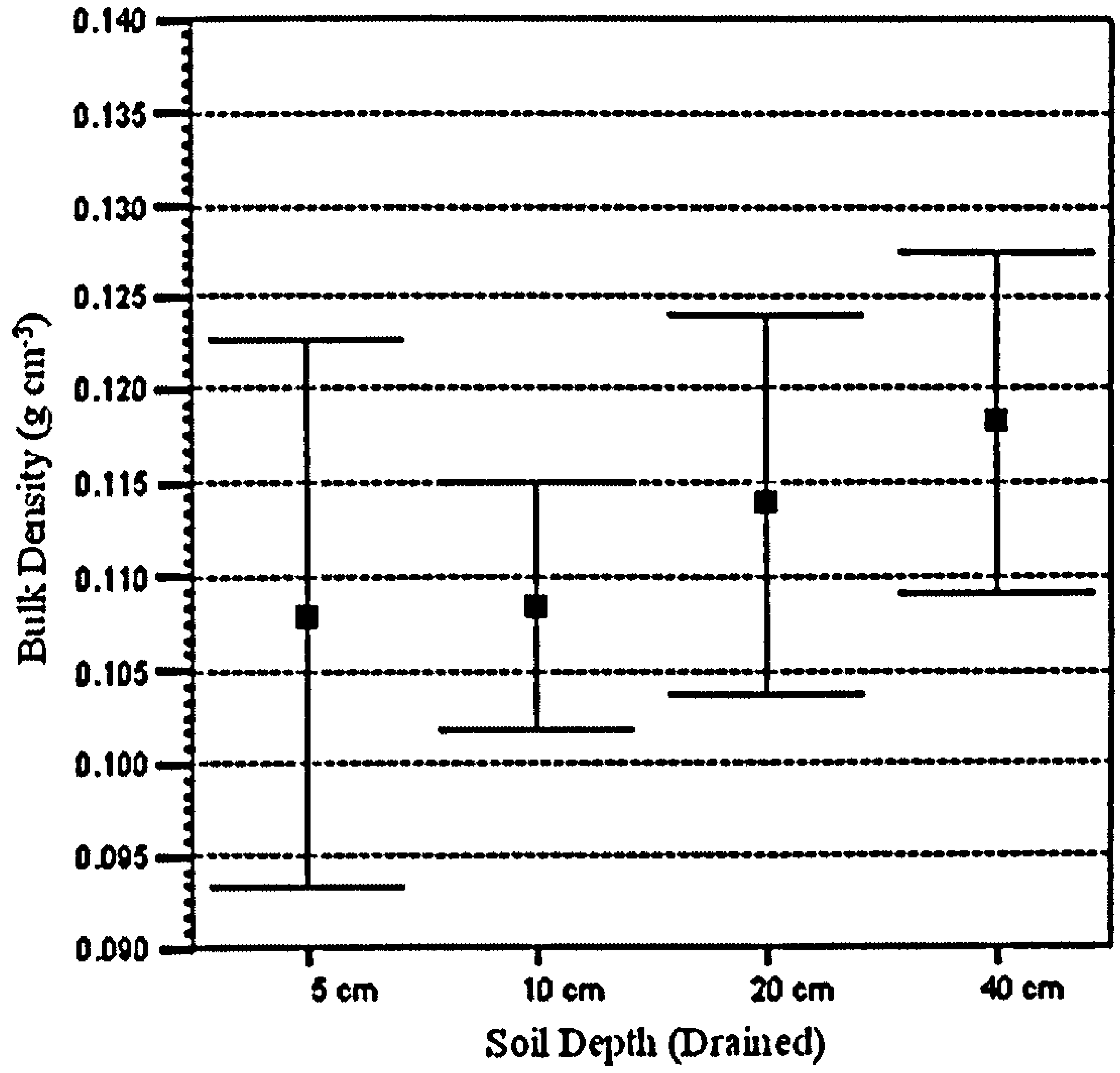


Figure 7.20 Mean bulk density values by soil depth for the drained site, ± 1 SE of the mean.

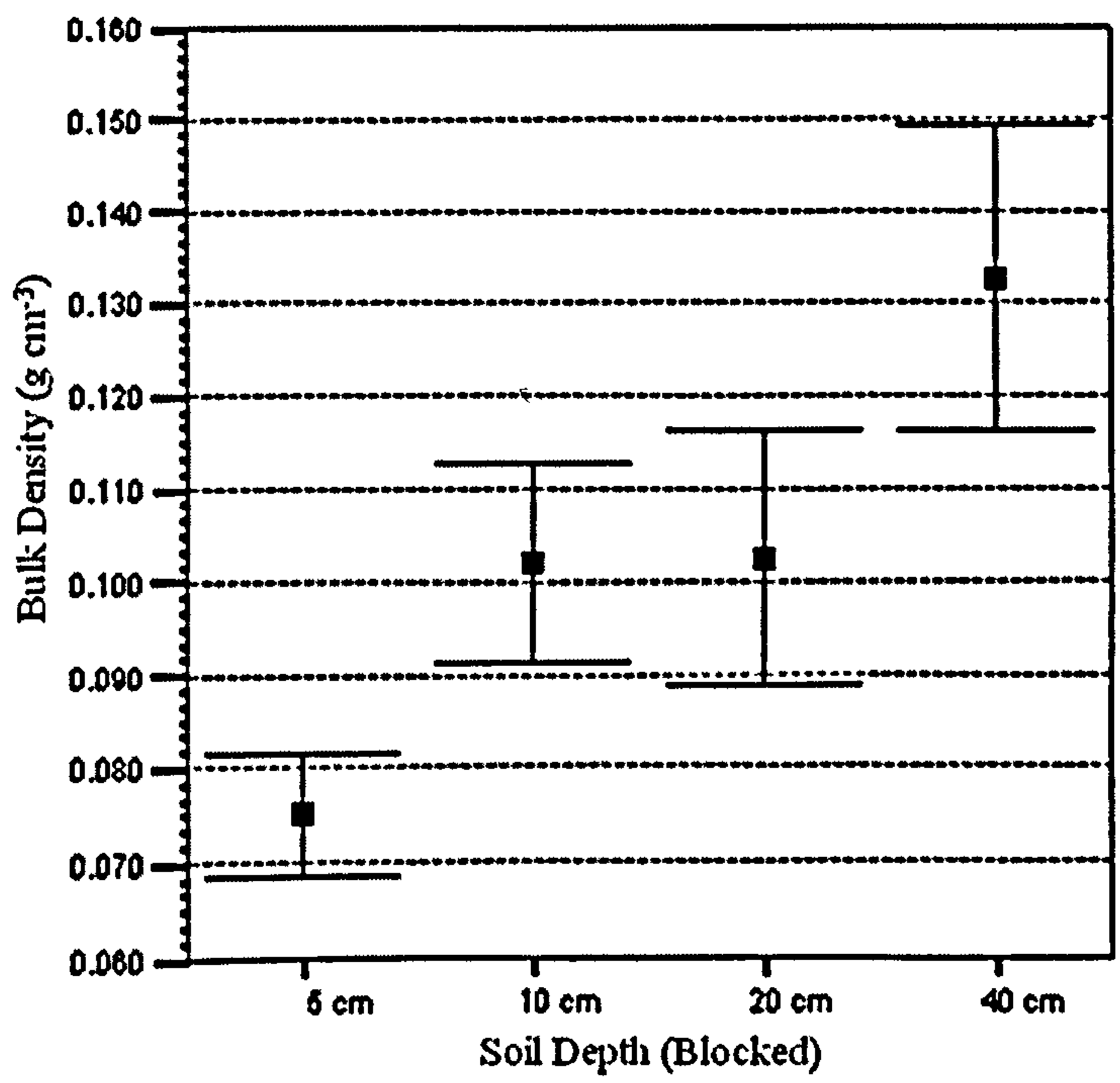


Figure 7.21 Mean bulk density values by soil depth for the blocked site, including ± 1 SE of the mean.

7.4. DISCUSSION

The mean daily water table depth at the intact site was -4.25 cm, and the water table was found to reside within the top 10 cm of the peat surface for approximately 80 % of the time during the period December 2004 to July 2006. The maximum mean daily water table depth observed was -13.87 cm on June 7th 2006, whilst the greatest depth recorded at any one of the individual dip-wells located across the transect was -20.42 cm. However, such an extended depth of water table drawdown was recorded very infrequently, and generally only occurred during short periods over the summer months in response to a reduction in total daily rainfall. This relates well with the assumption made in Chapter 4 in which it was assumed that the water table did not generally exceed 10 cm depth. It also corresponds well with Holden (2006) who observed that the water table in a neighbouring area of undisturbed blanket peat at Oughtershaw remained within 10 cm of the surface for 75 % of the time during the period December 2002 to December 2004, and that again it was only during the summer months that the water table declined to levels below this, with a maximum depth recorded of 25 cm. Furthermore, the data relates well to the findings of Evans *et al.* (1999) who observed that the water table depth at Moor House NNR remained within 5 cm of the surface for approximately 83 % of the time; and Price (1997; 1996) who observed a mean water table depth of -5 cm in an undisturbed Canadian *Sphagnum* peat bog.

As expected by the enhanced levels of DOC and colour production and microbial activity observed at the drained site in Chapters 4 and 6, the mean daily water table depth at this treatment was found to be significantly lower than that of the intact site, with the mean reduced by nearly 10 cm to -13.87 cm, whilst the maximum mean depth to the water table was nearly double at -27.29 cm, which was recorded on September 7th 2005. This corroborates the work of Ivanov (1981) who identified that a lowered water table in response to peatland drainage resulted in the disintegration of the peat through the desiccation of the soil, and that associated increases in temperature and biological activity lead to the enhanced decomposition of organic matter. The water table at the drained site also spent a far greater proportion of time below the surface compared to the intact site, being located at or above 10 cm of the peat surface for only 35 % of the time during the sample period. This corresponds well with Ingram (1992) who compared drained and un-drained areas of a raised mire in Finland and found that the variability of the water table depth was much greater with drainage, even though on occasion the water table was almost at the same height as in the un-drained area; and Mawby (1995) who observed that at a *Sphagnum*-dominated peat in Cumbria, the water table at a cutover bog fluctuated highly between -10 cm during wet periods and -80 cm during drier periods, whilst in a neighbouring area of undisturbed peat the water table was relatively stable exhibiting an annual fluctuation of ≤ 20 cm.

When the height of the water table was analysed along the length of the drained transect, it was found to be significantly lower at each of the eight dip-wells compared to the corresponding points located at the intact site. It was also observed that the greatest area of influence for water table drawdown occurred at the dip-well located immediately (≤ 1 m) down-slope of the ditch, where the mean water table depth was reduced by more than 11 cm relative to the two dip-wells located ≤ 2 m either side, and 23 cm relative to the corresponding point located along the intact transect. This was used to establish (obviously within the confines of a 60 m transect, where measurements were made at varying intervals along its length) that the water table drawdown extended for at least 15 m up-slope and as far as 34 m down-slope of the ditch, and that the greatest area of influence (e.g. greatest water table depression) was immediately (1 m) down-slope. This corresponds well with McLay *et al.* (1992) who studied the effects of drainage and cultivation in a sedge and *Sphagnum*-dominated peat in New Zealand, and found that a lowered water table was observed up to 50 m away from the ditch; and Stewart and Lance (1991) who examined the effects of peatland drainage on the water table at Moor House and observed an asymmetrical zone of drawdown around the ditch, with the lowest water table depths recorded down-slope.

The extent of water table drawdown recorded herein appears to be far greater than that observed by Stewart and Lance (1991) who identified that although the mean water table depths closest to the drains were lower than at places further away, the drawdown was slight and confined to a zone of less than a few metres either side of the drain, with a maximum water table depth recorded of only -5.37 cm. However, it is thought that the results of Stewart and Lance (1991) should be treated with caution given that i) measurements at the drained site were taken daily over a short 20-day period, whilst measurements at control plots were taken over an even shorter period of 11 days; ii) the spacing between the drains was far smaller at approximately 15 m, compared to ~45 m at Oughtershaw, and thus with respect to the sample design, water table drawdown would only be effective up to a distance of 7 m either side of the ditch anyway; and iii) the climate at Moor House is generally wetter and this may have some influence on the ability to which the drains may lower the water table. Furthermore, it is unlikely that the same degree of water table drawdown would be recorded given that the efficiency of drainage to reduce the level of the water table is influenced by the depth of ditching, the distance between ditches, the topography, and the structural and infiltration properties of the individual peat soils (Armstrong 2000; Boelter 1972). For example, although water table drawdown is normally greatest nearest the ditch and generally diminishes with increasing distance, the actual distance to which there is effective drawdown varies, with Boelter (1972) observing that in a peat bog consisting of moderately decomposed peat materials, the influence on the water table was generally limited to 5 m distance from the ditch, whereas in a peat that was dominated by more fibric un-decomposed peat, the ditch was more effective in lowering the water table up to 50 m away, due in part to a greater rate of hydraulic conductivity.

In contrast, drain blocking appears to be a highly successful technique for restoring the height of the water table, with a mean daily water table depth of -9.30 cm found to be significantly higher than that of the drained site, which relates directly to the reduced levels of DOC/colour production and microbial activity observed for the site in Chapters 4 and 6. In addition, the maximum water table depth of -20.10 cm, recorded on July 11th 2005, was found to be 26 % lower than that observed at the drained site, whilst the greatest depth recorded at any one of the dip-wells located along the transect was also lower at -28.24 cm. Furthermore, it was found that the water table at the blocked site spent far less time below the surface compared to the drained site, being located at or above 10 cm depth for 57 % of the time during the sample period. These findings correspond well with those of Worrall *et al.* (2007a) who assessed the effectiveness of drain blocking in an upland blanket peat catchment in the Forest of Bowland, northern England and found a significant increase of 9 cm in the water table depth of peat located adjacent to drains that had been blocked compared to drains that remained open; and Schlotzhauer and Price (1999) who investigated soil water dynamics in a Canadian cutover peat and found that ditch blocking and the installation of an open water ditch-reservoir enhanced the wetting of adjacent peat and improved the water table depth and soil moisture content.

Although the height of the water table was found to be restored with respect to the drained site and the extent of the up-slope water table drawdown was greatly reduced, the mean daily water table depth at the blocked treatment was still significantly lower than that of the intact site, and the spatial extent of the down-slope drawdown was the same as that recorded at the drained site. In addition, the spatial and temporal variability of the water table was greater at the blocked site, exhibiting a far greater range of values and a maximum drawdown that was 8 cm lower than that recorded at the intact site. However, similar results were also found by Mawby (1995) and Price (1997; 1996) who observed that although ditch blocking successfully raised the height of the water table, water levels were still lower and more variable compared to areas of undisturbed peat and continued to drop quickly during dry spells in the summer, even on areas where the bog surface was level or shallow and where surface flooding was maintained over most of the year.

The relatively high level of variability between the water table depth recorded at the intact and blocked sites suggests that either there has not been enough time since restoration was initiated (~5 years previously) to allow for a full water table recovery, or that there may have been permanent changes to the structural and/or infiltration characteristics of the peat. The latter of which corresponds well with the findings of Dasberg and Neuman (1977) who noted that the properties of peat changed dramatically when it became partially de-saturated; and Price (1996) who concluded that few Canadian peatlands revert back to their natural state, as drainage alters the local hydrology, microclimate and physical peat properties such that changes to the soil matrix cause the specific yield of the peat to reduce, which results in exaggerated water table changes and a greater matrix suction in restored bogs. In addition, Evans *et al.* (1999) and Holden and Burt (2002b) observed a depressed rate of water table recovery at the end of a prolonged period of water table drawdown and suggested that this indicated the peat had undergone physical changes as it dried out; whilst Schouwenaars (1993) assessed the hydrological effects of peatland restoration and found that the hydrology of bog relicts differed from undisturbed peat, as the surface layers consisted of moderately to strongly humified peat as a result of drainage and peat cutting, which resulted in relatively high water table fluctuations.

The total number of days during the study period in which total surface saturation was recorded at the intact site, and thus the proportion of time in which saturation-excess overland flow could be generated, was 107 out of 564 (i.e. 19 % of the time). This relates well with the high percentage level of occurrence of OLF (93 %) that was recorded between the monthly visits made to the site. It also corresponds well with the findings of Holden (2006) who observed that 74 % of runoff produced at Oughtershaw occurred in the topmost surface layers, at depths ≤ 1 cm; and Holden and Burt (2003c) who noted that over 80 % of runoff at Moor House was produced as saturation-excess OLF. Such high levels of surface runoff are common in undisturbed peat soils due to the low depth to the water table and its unique two-layered structure, which both help to regulate the storage and discharge of water such that, when the water table is high the majority of flow occurs through and over the relatively permeable upper acrotelm layer and thus peat readily sheds excess water; yet the high specific yield allows this to occur with a relatively small drop in water table depth (Bay 1969). For example, Holden and Burt (2002a; 2002c) noted that most runoff is produced within the top few centimetres of peat, with saturation-excess OLF being rapidly generated in undisturbed blanket peat soils due to the typically high antecedent water tables in combination with the rapid rate of infiltration into the acrotelm layers. Furthermore, Bay (1970) and Chapman (1965) observed that runoff production ceased at approximately the same water table elevation each year, such that water above this height was available for surface and near-surface runoff, whilst water below was retained in the peat; whilst Evans *et al.* (1999) noted that the antecedent water table depth had a great influence on the level of runoff production, observing a negligible hydrograph response whilst the water table was low, but finding that as soon as enough water infiltrated the soil to raise the water table to within 5 cm of the surface, there was a rapid hydrograph response.

In contrast, the lower water table at the drained site resulted in a significant reduction in the level of surface saturation, with the water table only being recorded at or above 0 cm on 17 days out of the 564 day sampling period, which relates well with the 32 % reduction in the occurrence of OLF recorded, relative to the intact site. It also corroborates Holden (2000) who identified that drainage reduced the level of OLF generation, particularly at sites located immediately down-slope of a drain, and suggested that this was likely to be related to the reduction in the supply of water from up-slope areas due to the interception caused by the drain itself. In addition, Rennes *et al.* (1976) studied the effect of mole drainage on soil moisture and surface runoff from a Tokomaru silt loam and found that the level of OLF was reduced at the drained site by between 25 and 50 % compared to an undrained soil; and Holden and Burt (2002a; 2002b) observed that during warm and dry weather, rainfall tended to infiltrate more readily into the soil to the extent that steady-state surface runoff rates were reduced and more flow took place within the peat, albeit at shallow depth. Meanwhile at the blocked site, although the occurrence of OLF was still found to be significantly lower than that observed at the intact site, the water table restoration appears to have improved surface saturation levels sufficiently to increase the potential for OLF generation. The water table was found to be at or above 0 cm at the blocked site on 56 days during the sample period, which resulted in a 23 % increase in the occurrence of OLF relative to the drained site. This supports the findings of Shantz and Price (2006) who observed that following ditch blocking at a Canadian peatland, rates of OLF generation and surface ponding were enhanced relative to the drained peat.

The reduction in OLF at the drained and blocked sites corresponds well with the fact that during periods of extended water table drawdown a greater proportion of runoff occurs as subsurface flow, which travels at greater depths through the peat soil layers where there are lower rates of permeability and hydraulic conductivity, and is thus retained in the soil for a longer period of time (Boelter 1965). This implies that drainage may help to reduce the "flashy" hydrological response that is typical of upland blanket peat catchments by providing extra soil storage capacity for rainwater, which would reduce the volume of surface flow during the early stages of a storm and slow down the transfer of water to rivers and streams (Baden & Eggelsmann 1968; Burke 1975a). However, drainage may actually speed up the delivery of water as the ditches may act as high velocity conduits, whilst in the long term as the peat dewaters it is also liable to subside so that any temporary increase in storage capacity may be lost and the catchment reverts back to its flashy nature with a concomitant increase in flood risk (Holden *et al.* 2006; 2007). In contrast, it appears that peatland restoration in the form of drain blocking may help alleviate these negative hydrological impacts given the fact that the peat dams have been found to help reduce both the speed and volume of water being transferred along the drainage ditches by up to 70 % (e.g. Worrall *et al.* 2007a).

Infiltration measurements identified that subsurface runoff production at the intact site was dominated by macropore flow, with over 74 % of infiltration observed to occur at water tensions less than 3 cm, and thus through pores greater than 1 mm in diameter. Although these values appear high, they support the findings of Silins and Rothwell (1998) who observed that 84 % of subsurface flow in a Canadian peat occurred within pores >0.6mm in diameter; and Baird (1997) who identified that approximately 64 % of subsurface flow in a lowland fen peat in Somerset, England, occurred though macropores that were >1 mm in diameter. Furthermore, Holden *et al.* (2001) observed that macropore flow was a significant pathway for runoff production in the upper soil layers of the blanket peat at Moor House. However, they found the proportion of flow occurring through macropores at the peat surface was far lower at 37 %; although the level they observed at 5 cm depth appears to be more comparable at 48 %

Although it is uncertain as to why the reported range in the level of macroporosity is so large, it is thought that it may relate to the inherent variability in the soil properties of the individual peats on a site-specific basis. For example, the slightly lower values identified by Baird (1997) may be explained by the fact that ombrotrophic peat soils tend to have higher intracellular water contents (i.e. water held in macropores) than minerotrophic peats due to differences in the structure and morphology of the various plants present at each (Hobbs 1986). In contrast, the far higher level of macroporosity identified herein compared to that observed by Holden *et al.* (2001) may relate to the degree of humification. For example, un-humified or fibric peat has a higher tensile and shear strength and thus has a greater water content and void ratio compared to more humified/decomposed peat, meaning it has a greater proportion of large pores that are easily drained and offer little resistance to water flow, whereas although more humified peat can exhibit porosities up to 90 %, the pores are generally far smaller (Boelter 1972; Hobbs 1986; Price *et al.* 2003).

As discussed previously, the lowering of the water table at the drained and blocked sites appears to have affected the structural and infiltration characteristics of the peat. This was confirmed when the proportions of macropore flow were compared between sites, where it was found that values at the drained and blocked sites were reduced by 8 % and 14 % respectively relative to the intact site. Thus, in addition to an increase in the volume of runoff produced as subsurface flow at the drained and blocked sites (as evident by the lowered water table and subsequent reduction in OLF) it appears that a greater proportion of the water moving through the peat travels through smaller pores in the soil matrix compared to the intact site. This corroborates the findings of Burghardt and Ilnicki (1978), Egglesmann (1975) and Silins and Rothwell (1998) who observed that a lowering of the water table associated with peatland drainage resulted in the subsidence of the surface layers and an associated collapse of readily drainable macropores, which subsequently increased the residence time of percolating water. For example, Silins and Rothwell (1998) observed that drainage resulted in the severe shrinkage and consolidation of a peat soil, causing the upper soil layers to subside, which reduced the proportion of water travelling though pores $\geq$ 0.6mm in diameter from 84 % to 50 %, whilst concurrently increasing the volume of flow through pores 3-30 μm in diameter.

In addition, Price and Schlotzhauer (1999) and Price *et al.* (2003) found that water table lowering in a mined peatland caused surface subsidence, which was shown to be partly due to the shrinkage of the soil above the water table and partly due to the compression of the lower peat layers of saturated peat, and a reduction in the size of the soil pores; whilst Ingram (1992) found that in drier conditions rates of aerobic decomposition accelerate and vertical subsidence and compaction can occur, which increases the proportion of space occupied by solids and thus reduces the volume of fast-draining macropores and the level of permeability. Furthermore, McLay *et al.* (1992) observed that a greater amount of water in a drained soil was held at high suctions and suggested that this occurred in response to an increase in the proportion of meso- and micropores; and Campeau (1996) found that attempts to restore the hydrology of cutover peatlands are generally unsuccessful due to the high levels of peat compaction and oxidation, and enhanced matrix suction.

Therefore, it seems the water table drawdown observed at the drained and blocked sites exposes the peat to volumetric change mechanisms, which seriously affects peatland hydrology and runoff production, and involves a sequence of events that include oxidation, primary consolidation, shrinkage, secondary compression and subsidence (Hobbs 1986). Primary consolidation is usually the major response of a soil to increased loading after drainage, and occurs because the void space within the soil is reduced as the weight of the overburden (i.e. the layer of drained peat) compresses the wet soil beneath, leading to the expulsion of water from the diminishing pore spaces and the structural realignment of particles (Fetter 1994; Ratcliffe & Oswald 1988). Meanwhile, compression may result in greater (vertical) capillary flow, whereby smaller pores in the unsaturated zone exert a stronger pull on the residual water compared to uncompressed peat at a similar water content; and is followed by the process of subsidence that arises when the organic components of the peat oxidise to gaseous compounds and water leaving only the mineral component as residue, which results in the remaining soil particles becoming more tightly packed (Ratcliffe & Oswald 1988; Schlotzhauer & Price 1999). Evidence of subsidence and consolidation in drained peatlands is provided by Minkkinen and Laine (1998) who measured the rate of subsidence 60 years after drainage in 273 peatland sites located throughout Finland, and found that on average the peat surface had subsided by about 22 ± 17 cm; and Price *et al.* (2003) who identified that drainage and the removal of the acrotelm layer resulted in surface subsidence of up to 3.7 cm y^{-1} m^{-1} shortly after drainage due to compression, whilst in the long-term rates of up to 0.3 cm y^{-1} m^{-1} occurred in response to further compression and oxidation.

It is thought that the enhanced rate of subsurface flow in conjunction with the reduction in macroporosity at the drained site is likely to have increased the residence time of percolating waters, such that, in addition to the enhanced levels of DOC and colour produced via the stimulated rate of microbial activity, there is a greater level of soil-water interaction, which results in the greater mobility and transportation of these decomposition products relative to the intact site. For example, Luxmoore *et al.* (1990) Jardine *et al.* (1990a) and Ross (1995) identified that because macropores have a small surface area they behave largely as physical conduits without much effect on water quality, whereas mesopore and adjacent micropores that flow through the peat matrix have a greater ability to supply solutes as the longer flow paths through the soil body and greater pore water retention times mean there is greater opportunity for percolating water to interact with the greater surface area of mesopores, and the non-draining micropores that contain antecedent soil water.

In contrast, at the blocked site it is thought that the initial response to the heightened water table in conjunction with the reduction in macropore flow may be a flush of DOC/colour from the smaller pores and the loss of the more labile (un-coloured) DOC components, as these are preferentially channelled through the soil relative to the more refractory (coloured) faction, which is more strongly adsorbed to the soil (Jardine *et al.* 1990b). However, in the long-term once the store of decompositional products has been depleted, DOC and colour values are likely to be reduced given that i) there will be a reduced rate of production as the source of organic matter has been severely degraded and the rate of microbial activity has been reduced and ii) there will be less accumulation of decompositional products given the elevated soil-water interactions in response to the enhanced levels of flow through the soil matrix, relative to the intact site.

The reduced levels of macroporosity at the drained and blocked sites are however in direct contrast to the observations of Evans *et al.* (1999) and Holden and Burt (2002b) who suggested that, although the aeration of peat may result in significant changes to soil structure, the shrinkage and cracking associated with surface drying would potentially result in more rapid levels of infiltration and vertical water movements through the development of macropores. For example, Holden and Burt (2002b) found that experimentally manipulated soil cores extracted from Moor House and exposed to drought conditions experienced a reduction in moisture content and an increase in the level of macroporosity within the surface layers, which resulted in preferential flow extending to greater depths than the controls. However, it is thought that because Holden and Burt (2002b) studied laboratory manipulated soil cores, they may have experienced different conditions to those existing in the field given that drainage of the lower peat layers is probably more restricted under field conditions as water cannot freely flow off. Therefore, in field saturated peat with less lateral flow additional macropores might not emerge under drought conditions or they may close more rapidly afterwards, whilst rapid flow through macropores under laboratory conditions may enlarge or sustain preferential flow paths.

In addition, Holden and Burt (2002b) only exposed their peat cores to a four week experimental drought, whereas the drains at Oughtershaw were dug over 40 years previously. Thus, it may well be that the initial response of a de-saturated peat is the shrinking and cracking at the soil surface and an increase in macroporosity; but in the long-term the de-watering of the peat and increasing weight of overburden is likely to result in a significant amount of subsidence and compaction, and thus an overall reduction in macropore flow. Furthermore, the soils at Oughtershaw are likely to behave differently to those at Moor House given the initial differences in the relative proportions of macropore flow. This is because a relatively un-humified peat, which exhibits a high proportion of void spaces and thus macroporosity, undergoes a substantial level of primary consolidation and subsidence in response to water table drawdown, whilst more amorphous, humified peat, which has a greater proportion of smaller pores, tends to shrink and crack more because its fibres are not aligned in any way (Hobbs 1986; Okrusko 1995; Ratcliffe & Oswald 1988).

The findings presented herein also oppose the work of Holden (2005) who used a ground penetrating radar (GPR) system to survey 160 British blanket peat catchments for soil pipe (large macropores) networks and found that land drainage exerted the most significant control on the level of pipe frequency. However, such differences are not unexpected given the different methods and sampling approach undertaken, as a tension infiltrometer used at the soil surface does not have the same ability as a GPR system to locate networks of soil pipes that are situated deep within the soil profile, and which often exhibit no surface expression.

The mean rate of surface hydraulic conductivity at the intact site was 1.07×10^{-3} cm s^{-1}, and values ranged over an order of magnitude from 4.97×10^{-4} to 1.50×10^{-3} cm s^{-1}. This corresponds well with a large range of values reported in the literature, including Smith (1956) who found for an intact *Sphagnum* peat hydraulic conductivity rates were in the order of 6.6×10^{-3} cm s^{-1} to 2.8×10^{-1} cm s^{-1}; Baden and Eggelsmann (1963) who observed 5×10^{-4} cm s^{-1} for a *Sphagnum* peat; Boelter

(1965) who recorded 4 x 10^{-2} cm s^{-1} for an un-decomposed *Sphagnum* peat; Galvin and Hanrahan (1967) who recorded 1.1 x 10^{-5} cm s^{-1} for a blanket bog at 30 cm depth; Dai and Sparling (1973) who observed 6 x 10^{-3} cm s^{-1} for an ombrotrophic *Sphagnum* bog at 50 cm depth; Holden *et al.* (2001) who recorded 3.73 x 10^{-4} cm s^{-1} at the surface of a *Sphagnum* covered peat; and Romanov (1968) who observed 3.1 x10^{-3} cm s^{-1} at *Carex*-dominated peat in Russia. The relatively large range of values recorded at the intact site also corroborates Holden and Burt (2003a; 2001) who observed that the hydraulic conductivity of blanket peat can vary over several orders of magnitude over just a few meters vertically or horizontally and that measurements are rarely within one order of magnitude error bands.

When the rates of hydraulic conductivity were compared between sites it was found that whilst the intact site had a far higher level of macropore flow compared to the drained site, there was little difference in the rate of hydraulic conductivity between the two treatments, with the drained site exhibiting a mean of 9.89 x 10^{-4} cm s^{-1}, and a slight lower range of values from 6.17 x 10^{-4} cm s^{-1} to 1.51 x 10^{-3} cm s^{-1}. Although there are only a few published records of hydraulic conductivity in drained peat soils, the values identified in this study correspond relatively well with Rycroft (1971) who observed rates of 3.1 x 10^{-3} cm s^{-1} for an overgrown ditch, and suggested that this was typical of hydraulic conductivities in marginal situations; and McLay *et al.* (1992) who recorded a rate of 4 x 10^{-4} cm s^{-1} at the surface of a drained *Sphagnum* peat. In addition, the slight reduction in the range and mean rate of hydraulic conductivity at the drained site relates well with Rycroft (1975) and Boelter (1972) who observed that humified peat exhibited lower hydraulic conductivity rates compared to relatively un-decomposed peat; and Price *et al.* (1999) who suggested that if drainage results in significant shrinkage, there would be a reduction in hydraulic conductivity.

In contrast, although the blocked treatment exhibited the lowest proportion of macropore flow, its rate of hydraulic conductivity (1.56 x 10^{-3} cm s^{-1}) was found to be significantly higher than that of the intact and drained sites, whilst the range of values were slightly lower at 9.8 x 10^{-4} cm $s^{-1}$to 2.44 x 10^{-3} cm s^{-1}. Although somewhat complex, this suggests that even though there has been a reduction in the volume of free draining macropores, there is an even greater tendency for subsurface flow to occur through the soil matrix due to an increase in meso- and micropore flow.

Furthermore, it bears some resemblance to the findings of Holden and Burt (2001) who observed that for a bare peat, rates of hydraulic conductivity were higher than at vegetated sites, and suggested that it may be logical to relate the greater flux at the surface to a greater level of macroporosity given that the bare surface layer would be exposed to process of desiccation and cracking. However, Holden and Burt (2001) actually found that the level of macroporosity at the bare peat was not significantly different to that observed for a vegetated peat, and subsequently concluded that the propensity for matrix flow in the un-vegetated surface layers had increased.

The relatively high rates of hydraulic conductivity recorded at all three sites are equivalent in value to infiltration rates of 38.5 mm h^{-1} for the intact site; 35.6 mm h^{-1} for the drained site; and 56.2 mm h^{-1} for the blocked site. Given the fact that, during the period of study where rainfall data was available (December 2004 to March 2006), no rainfall recorded ever exceeded 35 mm h^{-1}, this suggests that the generation of infiltration-excess overland flow in response to excessive rainfall is likely to be extremely rare at Oughtershaw; and thus the majority of surface runoff is likely to be produced as saturation-excess overland flow. This corresponds well with the findings of Holden *et al.* (2001) who demonstrated through the use of a tension infiltrometer that infiltration-excess overland flow was unlikely to be a common runoff-generating mechanism in blanket peat soils as the near-surface layers of peat at Moor House were found to readily transfer water away from the surface.

The mean bulk density at the intact site was 0.108 g cm^{-3}, which agrees relatively well with the work of Boelter (1976) who observed a bulk density of 0.153 g cm^{-3} in a moderately decomposed peat; and Silins and Rothwell (1998) who observed a value of 0.08 g cm^{-3} in an un-drained peat. However, they are far higher than those reported by Romanov (1968) who observed values in the range of 0.017 to 0.076 g cm^{-3} for a Russian *Carex*-dominated bog. Again, the high degree of variability is thought to relate to the inherent site differences given that bulk density has been found to vary in response to factors such as climate, botanical composition, pore structure, level of decomposition, organic matter content, moisture content and degree of saturation (Boelter 1968, 1976; Hobbs 1986; Laine *et al.* 1994).

Values of bulk density also appeared to increase with soil depth at the intact site, from 0.095 g cm^{-3} at 5 cm to 0.121 g cm^{-3} at 40 cm. This corresponds well with Holden and Burt (2001) who found that bulk densities at Moor House ranged from 0.15 g cm^{-3} at the surface to 0.18 g cm^{-3} at 20 cm depth, and gradually increased with depth to 0.27 g cm^{-3} by 50 cm. Bulk densities are generally higher at depth due to the reduction in root channels and soil-dwelling organisms, as well as the greater degree of compaction caused by the weight of the overlying soil layers (Brady & Weil 2002). However, in addition to the increase in bulk density with depth, there was also a distinct step-like increase between 10 and 20 cm. It is thought this relates directly to the location of the water table at the intact site, which was found only to exceed a depth of 10 cm for less than 20 % of the time, and given the fact that the bulk density in the acrotelm layer is generally lower than that of the catotelm (Van Seters & Price 2002), it provides further evidence that the acrotelm-catotelm boundary resides somewhere between 10 and 20 cm depth.

The mean bulk density at the drained site (0.112 g cm^{-3}) was slightly higher than that recorded at the intact site, and there was far less variation in values between soil depths, with values found to range from 0.108 g cm^{-3} at 5 cm to 0.118 g cm^{-3} at 40 cm. This corresponds well with the lowering of the water table and suggests that the soil layers at the drained site are more compacted and thus more homogenous as a result of subsidence, which supports the observed reduction in macropore flow. In addition, the lack of definition in bulk density values between soil depths also corresponds well with the apparent lowering of the actrotelm-catotelm boundary, as previously identified in Chapter 4. The results also corroborate well with McLay *et al.* (1992) Price (1997; 1996), Rothwell *et al.* (1996) Silins and Rothwell (1998) and Schlotzhauer and Price (1999) who all found that peatland drainage was followed by the oxidation and irreversible subsidence of the surface layers, which resulted in an increase in bulk density and water retention capacity, and a subsequent reduction in specific yield and hydraulic conductivity. In addition, Boelter (1968; 1972) observed that a humified peat exhibited a greater bulk density (0.17g cm^{-3}) and thus a lower hydraulic conductivity compared to relatively un-decomposed peat (0.07 g cm^{-3}), and suggested that peat soils exhibiting higher bulk densities tends to have a higher water retention due to the greater proportion of smaller pore spaces; whilst Holden and Burt (2001) found bulk densities were greater in an eroded peat (0.22 g cm^{-3}) compared to undisturbed site (0.15 g cm^{-3}), and suggested that the increase indicated that the exposed peat was of an older and more humified nature.

In contrast, the mean bulk density at the blocked site (0.103 g cm^{-3}) appeared to be reduced when compared to the drained site, especially in the top 5 cm where values were found to be significantly lower at the blocked treatment. Thus, it seems that although there may be consolidation of peat layers at depth, the uppermost soil layers at the blocked site appear to be less compact, which is likely to have resulted in the higher rate of hydraulic conductivity given the close association between the two (Ingram 1983). Although it is uncertain what has caused the lower bulk density and higher hydraulic conductivity at the blocked site, the fact that the main differences occur at depths $\leq$ 5 cm suggest that they may be caused by a regenerated level of *Sphagnum* growth in response to a heightened water table and greater level of surface saturation relative to the drained site. This is because during drainage the upper moss layer is replaced by a more compact and decomposed layer of peat (Schouwenaars 1993) and *Sphagnum* is known to exhibit a highly porous and relatively low density structure and thus a higher level of permeability compared to areas of more decomposed or herbaceous peat (Boelter 1964, 1965; Holden *et al.* 2001).

Bulk density was also found to increase with soil depth at the blocked site. However, the pattern of change was different to that observed for the intact and drained sites, as bulk density increased sharply between 5 and 10 cm (thought to be in response to a stimulated *Sphagnum* gowth) after which it remained relatively stable until a further step-like increase between 20 and 40 cm. This suggests that similar processes have been operating to those observed at the drained site, whereby water table drawdown has resulted in a lowering of the actrotelm-catotelm boundary; yet since volumetric changes are not easily reversed, it appears that the lowered boundary layer is unable to make a full recovery to its original height following water table restoration.

7.5. CONCLUSIONS

The water table was maintained very close to the peat surface at the intact site, exhibiting a mean daily depth of -4.25 cm, and was found to reside within the top 10 cm of the peat for approximately 80 % of the time during the period December 2004 to July 2006. The intact soil also exhibited a low bulk density and a relatively high and variable rate of hydraulic conductivity. In accordance with the shallow depth to the water table it appeared that the majority of runoff produced occurred over the peat surface as OLF, and due to the high rates of surface hydraulic conductivity, it is likely to be dominated by saturation-excess OLF rather than infiltration-excess OLF. Additional infiltration experiments revealed that subsurface runoff production was dominated by a high degree of macroporosity. This suggests that water movement both through and across an undisturbed blanket peat is relatively rapid, which relates well with the flashy hydrological regime often reported for undisturbed soils. Furthermore, as both OLF and macropore flow have relatively limited contact time with the soil matrix and decompositional products, these hydrological processes are thought to exert a limited effect on water quality with respect to the flux of DOC and coloured water.

The installation of drainage ditches was found to result in the lowering of the water table by nearly 10 cm, which caused a greater level of aeration of the surface layers as the water table was only found to reside within the top 10 cm of the peat for 35 % of the time during the sample period. The lowered water table and associated reduction in surface saturation significantly reduced the occurrence of OLF, which indicates that a greater volume of water is likely to be drawn down into the soil body relative to the intact site. In addition, the greater levels of aeration and the exposure of older and more humified peat layers also appears to have transformed the structure of peat, and consequently the manner in which runoff is produced. It seems that the greater level of aeration initiated a sequence of events that resulted in the subsidence, oxidation and compaction of the upper soil layers, which increased the level of bulk density and ultimately reduced the proportion of macroporosity within the soil. Therefore, as well as increasing the volume of water flowing through the soil body, it appears drainage also results in a greater proportion of the water moving through smaller meso- and micropores within the peat matrix. Subsequently, it appears that in conjunction with the enhanced levels of DOC produced via the elevated rates of microbial activity, the enhanced level of matrix flow relative to the intact site increases both the residence time of soil waters and the surface area over which they flow. This means that percolating waters have a far greater level of interaction with decompositional products, which is thought to enhance the mobility and transportation of DOC/colour.

Peatland restoration in the form of drain blocking was found to successfully raise the height of the water table by approximately 4 cm relative to the drained site, which subsequently increased the occurrence of OLF. However, the mean daily depth to the water table was still significantly lower and exhibited a greater degree of variability relative to the intact site, which suggests that the volumetric changes associated with drainage may have permanently altered the structural and infiltration properties of the peat, and thus the manner in which water is stored. It is thought a smaller pore size distribution, as a result of the reduction in macroporosity, has reduced the availability of water in the unsaturated zone due to the higher matrix potential, which results in seasonal water deficits having far greater influence on the water table compared to the intact site. The reduced level of macroporosity and build up of decompositional products in response to a lowered water table suggests that the initial response to the water table restoration may be a flush of DOC/colour and the preferential loss of the more labile components. Nonetheless, once the store of material has been depleted, DOC and colour levels are likely to be reduced relative to the intact site due to i) a reduction in production potential in response to the degradation of organic matter and a reduction in microbial activity; and ii) a slower rate of accumulation due to the elevated soil water interactions and pore water flushing initiated by the enhanced levels of subsurface flow through the soil matrix.

In light of the results highlighted in this chapter it is clear that peatland drainage and subsequent water table restoration may bring about a range of hydrological impacts. Further study is clearly required in order to determine whether the same processes operate in other drained and restored blanket peat catchments at both a national and international scale.

CHAPTER 8

CONCLUSIONS

8.1. THESIS OVERVIEW

Peatlands are important terrestrial stores of carbon and are a principal source of dissolved organic carbon to the fluvial environment. However, whilst they are often regarded as a net carbon sink, continued degradation in the form of peatland drainage is likely to result in a shift in the balance of the carbon budget, such that they become a net carbon source. Consequently, peatland restoration in the form of drain blocking currently represents one of the most significant technical challenges in peatland management and a large amount of effort and finance is currently being directed towards this ultimate goal. However, a great deal of this work has been carried out on a pragmatic or even an ad-hoc basis, and therefore there has been a distinct lack of process-based assessment. Hence very little is known about the influence of either drainage or drain blocking on the mechanisms likely to influence DOC and colour dynamics in blanket peat soils.

The research presented within this thesis has sought to bridge this gap in knowledge by undertaking a comprehensive plot-scale monitoring programme to allow greater insight into a range of chemical, biological, physical and hydrological processes operating in drained and restored blanket peat soils and how they influence the production and release of DOC and colour water. By drawing together the results from the field monitoring and laboratory measurements carried out in Chapters 4 – 7, this concluding chapter provides a summary of the major research findings, identifies any data limitations and highlights suitable areas for future research.

8.2. MAJOR FINDINGS WITH RESPECT TO RESEARCH AIM

Aim: To provide an intensive process-based assessment to establish the mechanisms involved in the modification of DOC and colour dynamics in a drained blanket peat, and the efficiency to which drain blocking is able to restore them, and consequently the influence of such changes in land management on carbon storage potential and water quality levels, relative to those currently observed in undisturbed blanket peat.

The results presented in the preceding chapters of this thesis have made significant improvements to our understanding of the complex relationships and interplay that exist between the biotic and abiotic processes in operation when a blanket peat soil is drained and subsequently restored. In Chapter 4, an assessment of the variability in DOC concentrations and the level of water discolouration in soil water solutions extracted from the three land managements was provided, which identified that the installation of drainage ditches resulted in a 35 % increase in both DOC and colour in comparison to an adjacent intact site that had not been drained. It was also observed that most of the additional DOC and colour produced appeared to come from peat deeper than 10 cm but shallower than 40 cm depth, with observed values at 20 cm enhanced by 60 % and 146 % relative to the intact treatment, suggesting the enhanced levels of production were likely to be in response to a lowered water table. In addition however, analysis of the C/C and E4/E6 ratios in Chapter 4 and the colour – carbon relationship in Chapter 5 highlighted the fact that significant variations in the composition of DOC occurred between the intact and drained sites, with the DOC at the drained treatment appearing slightly more humified in nature This again implied that a lowered water table may have disturbed fundamental DOC production and/or transportation processes operating within the peat, such as microbial activity and/or preferential flow paths.

Subsequent assessment carried out in Chapter 6 identified that rates of microbial activity were elevated by over 30 % at the drained treatment relative to the intact site; however, these differences proved insignificant at the 95 % confidence level (this is thought to relate to problems associated with the spectrophotometric method of analysis employed, in combination with a relatively small sample size). Therefore, it currently remains unclear as to whether the elevated DOC and colour values observed at the drained site are the result of an enhanced rate of production following the stimulation of microbial activity. Nonetheless, a significant increase in organic matter content was observed at the drained treatment relative to the intact site indicating an increased DOC production potential exists in the disturbed soil, which is assumed to result from an enhanced growth in microbial and/or vegetative biomass in response to a greater level of aeration associated with a lowered water table.

Additional hydrological assessment undertaken in Chapter 7 was able to confirm that the installation of the drainage ditches resulted in a significant reduction in the mean daily water table relative to the intact site, which corresponds well with previous research based in drained mires and cutover bogs (e.g. Ivanov 1981; Mawby 1992). Thus, it seems that the enhanced DOC and colour levels and modified DOC composition observed at the drained site, in particular those observed at a depth of 20 cm, can be related directly to the depth of the water table, which being lower is likely to have increased the level of oxidation in the surface peat and thus provided a means to stimulate microbial activity (e.g. Freeman *et al.* 2001b). Chapter 7 also identified that the lowered water table resulted in a reduction in surface saturation, which caused a significant decrease in the occurrence of saturation-excess OLF relative to the intact and implies that a greater volume of runoff is likely to be drawn down into the soil body at the drained site. Furthermore, it was found that the greater levels of aeration and the exposure of older and more humified peat layers appeared to transform the structure of the peat and the manner in which runoff is produced. It would seem that the greater levels of oxidation within the soil body initiated a sequence of events that resulted in the subsidence and consolidation of the upper soil layers, which subsequently caused the bulk density to increase and ultimately the proportion of surface macroporosity to be reduced. Therefore, as well as increasing the volume of water flowing through the soil, drainage also appears to result in a greater proportion of water moving through smaller meso- and micropores within the peat matrix, which is thought to increase both the residence time and the surface area over which soil waters flow (e.g. Luxmoore *et al.* 1990; Jardine *et al.* 1990a). As a result, percolating water at the drained treatment is likely to have a far greater level of interaction with decompositional products located within the soil body, and this is thought to enhance the mobility and transportation of DOC and colour relative to the intact site. A summary of the modifications made to these key processes as a result of drainage ditches is provided in a conceptual model presented in Figure 8.1; here it can be seen that this type of land management is highly detrimental, both to the sustainability of an important terrestrial carbon store and in the maintenance of ecologically sound water resources.

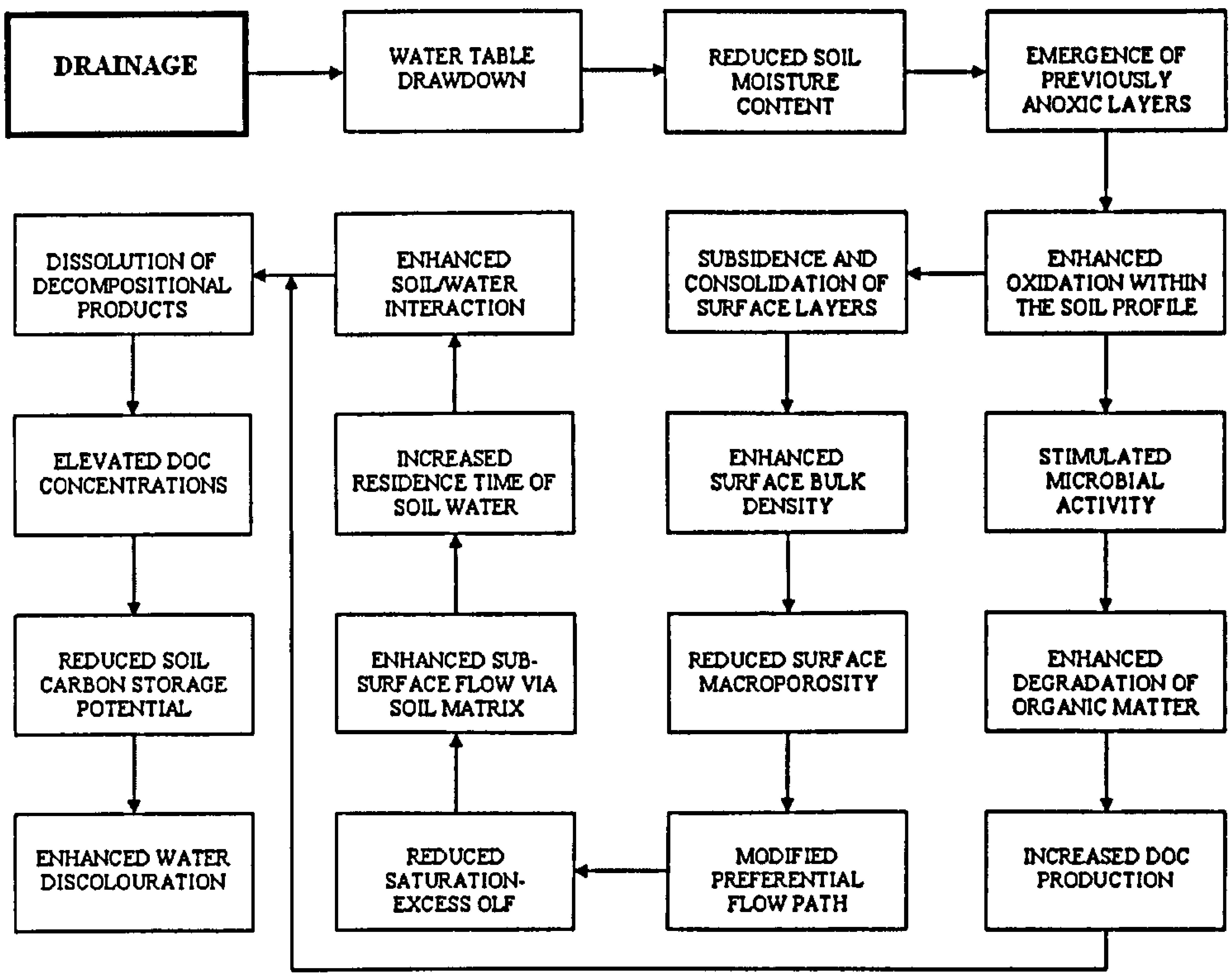


Figure 8.1 A conceptual model summarising the key processes influenced by the installation of drainage ditches in an upland blanket peat soil.

In contrast, drain blocking was found to be an effective technique for improving the carbon storage potential of a blanket peat soil and ameliorating upland water quality. For example, in Chapter 4 it was identified that blocking successfully reduced DOC concentrations and the level of discolouration in soil water solutions by 49 % and 32 % relative to the drained site, whilst values were also lower (31 % and 9 %, respectively) than those observed at the intact site. Furthermore, although there was a trend towards enhanced DOC and colour values with increasing soil depth at both the intact and drained sites, at the blocked treatment values remained low throughout the entire soil profile sampled. Meanwhile, assessment of the C/C and E4/E6 ratios in

Chapter 4 and the colour – carbon relationship presented in Chapter 5 indicated that the composition of DOC at the blocked treatment was markedly different to that observed at the intact or drained sites, for it exhibited a significantly greater amount of colour per carbon unit and appeared to be composed of older, more humified (and thus likely more recalcitrant) organic material. This implied that the process modifications associated with drainage may have caused permanent changes to the structural and infiltration properties of the peat, and thus the manner in which water (and therefore DOC and colour) is stored and transported within the soil.

Chapter 6 identified that there were significant differences in microbial activity rates between the blocked and drained sites with values almost 50 % lower at the blocked treatment, whilst rates were 31 % lower relative to the intact site (although this second comparison was not found to be significant at the $p = 0.05$ confidence level). Not only does this suggest that a reduced DOC production potential is present at the blocked site, it provides evidence against the commonly quoted hypothesis that an enzyme-latch reaction may be sustained in a peat that has been re-wetted following water table drawdown (e.g. Freeman *et al.* 2001b). Chapter 6 also identified that the organic matter content of the blocked peat was significantly lower than that observed at the drained and intact sites, which in conjunction with the altered DOC composition identified in Chapters 4 and 5 suggests that the re-saturation of the soil in response to a rising water table may have initiated a store exhaustion process whereby pore water flushing results in the degradation and removal of organic matter and thus limits the supply of DOC.

Hydrological assessment undertaken in Chapter 7 identified that drain blocking had successfully raised the height of the water table across the peat by an average of 4 cm relative to the drained site. Furthermore, it was found that the heightened water table increased both the level of surface saturation and the moisture content of the soil, resulting in a significantly greater occurrence of saturation-excess OLF. Nonetheless, the mean daily depth to the water table was found to be lower and exhibited a greater degree of variability compared to the intact site, whilst the proportion of macropore flow at the blocked treatment was significantly reduced. Consequently, it appears that the smaller pore size distribution resulting from the reduction in macroporosity reduces the availability of water in the unsaturated zone due to the higher matrix potential, which would cause seasonal water deficits to have a far greater influence on the water table compared to the intact site. In addition, the reduced level of macroporosity in association with the build-up of decompositional products due to the previously lowered water table suggests that the initial response to the water table restoration may be a flush of DOC and colour and the preferential loss of the more labile, un-coloured components. However, as seen in Figure 8.2 the reduction in microbial activity and thus DOC production potential, in conjunction with a slower rate of accumulation within the soil due to enhanced subsurface flow, means that once the store of organic material has been depleted, drain blocking is likely to be successful in reducing DOC and colour levels relative to those sites where drains remain unblocked.

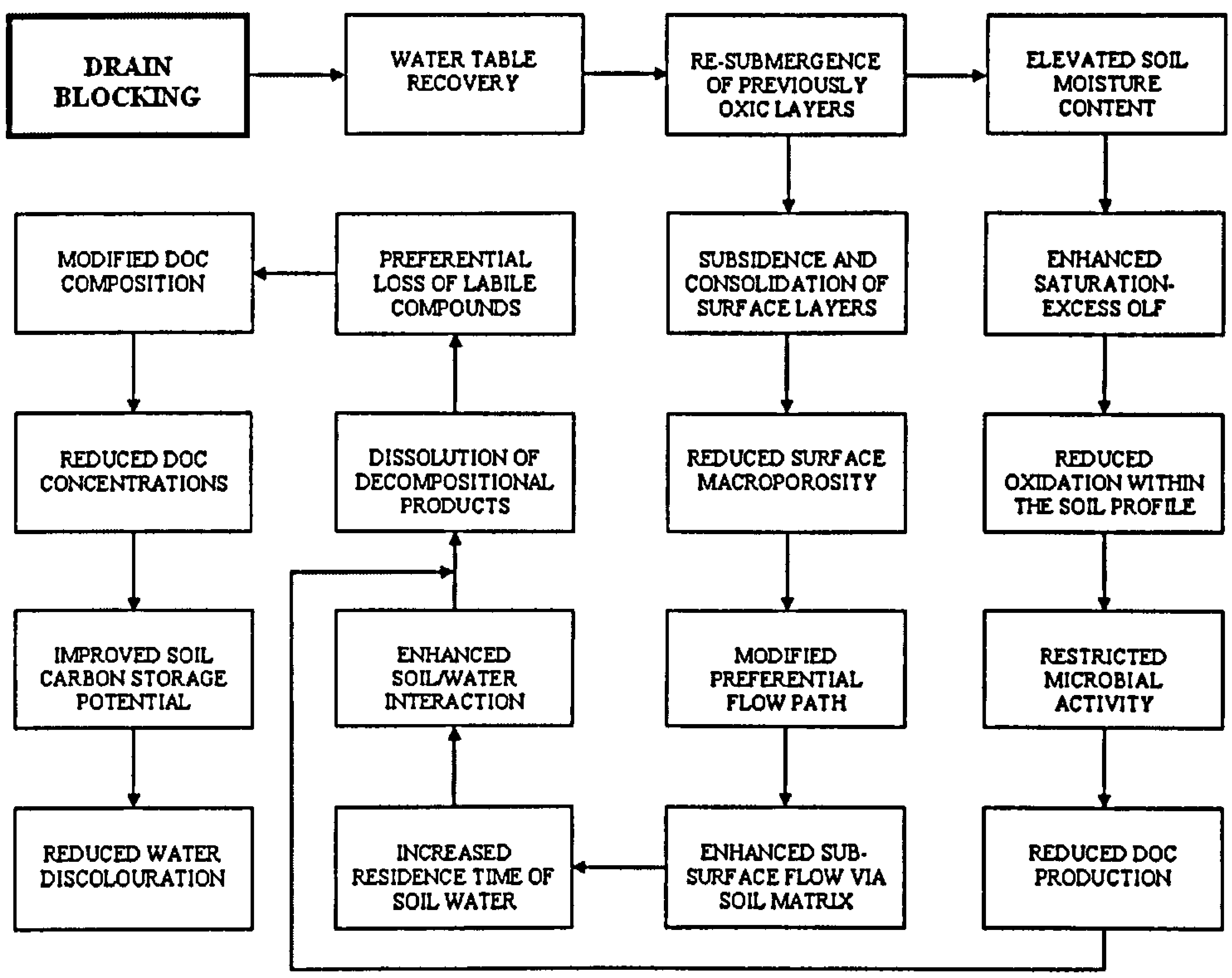


Figure 8.2 A conceptual model summarising the key processes influenced by the blocking of drainage ditches in an upland blanket peat soil.

8.3. MAJOR FINDINGS WITH RESPECT TO RESEARCH OBJECTIVES

Objective 1: Establish the effect of drainage and drain blocking on the DOC storage potential, within the soil profile of an upland blanket peat.

The increasing levels of degradation and associated ecosystem destruction observed in drained blanket peat soils are not desirable, with the installation of drainage ditches in the Oughtershaw Beck catchment found to significantly increase the concentration of DOC in soil water solutions by 35 %. When compared to the intact site, most of the additional DOC produced appeared to come from the peat that was deeper than 10 cm but shallower than 40 cm depth, with observed values at 20 cm enhanced by 60 %. This related well with the significantly lower water table observed at the drained site, which was found to have a mean depth of -14 cm below the peat surface. In contrast, a relatively successful restoration of the water table to a height of -9 cm at the drain-blocked site resulted in DOC concentrations being reduced by nearly 50 % compared to the drained site. Such a significant reduction, however, resulted in concentrations being lower than those recorded at the intact site, with values particularly reduced at a depth of 10cm. This suggests a process of porewater flushing of decompositional products operates in response to the heightened water table at the blocked site.

Further comparisons between the sites identified that the water table disturbance associated with these changes in land management alters not only the concentration of DOC, but also its composition and likely source. At the intact site, the DOC appeared to be produced from relatively young, labile fulvic material thought to be sourced from newly decomposing material located at the peat surface. However, at the drained and blocked sites significant variations in the E4/E6 and C/C ratios suggest that the DOC is supplied from older, more humified material dominated by more highly coloured refractory compounds, which is likely to be sourced from organic matter located deeper within the soil profile.

Drainage of blanket peat soils is therefore highly detrimental to the sustainability of a valuable terrestrial carbon store, and not only results in changes to the concentration of DOC released but also to the manner in which it is formed and stored. In contrast, drain blocking is actively encouraged as a form of peatland restoration as it was highly successful in reducing DOC concentrations and thus ameliorating many of the negative environmental impacts associated with drainage. However, it is apparent that even after restoration there are long lasting effects on the source and composition of DOC released, which will ultimately have some influence on its bioavailability and thus its transfer through the global carbon cycle.

Objective 2: Determine the effect of drainage and drain blocking on the quality and likely treatability of discoloured waters in an upland blanket peat.

Fluvial DOC is also an issue for the water industry, as most of the UK's upland blanket peat soils are located in major water supply catchments. The enhanced release of DOC and an associated rise in the level of water discolouration at the drained site is highly problematic for the production and distribution of drinking water as it significantly deteriorates water quality, and its removal is often the most expensive operation in terms of water treatment. Nevertheless, because the composition of DOC tended towards compounds that were more humic and therefore more hydrophobic in nature, it should still be possible to remove the DOC released from drained blanket peat soils using traditional techniques such as Ferric coagulation and acidification; although the higher DOC concentrations will undoubtedly mean a greater quantity of coagulant will be required.

In contrast, although the rewetting of a drained peat following water table restoration may result in an initial flush of DOC/colour (e.g. Worrall *et al.* 2007a); in the long-term it appears that drain blocking is a valuable catchment tool for improving the treatability of upland waters due to the significant reduction in the level of water discolouration. Furthermore, as the DOC released was found to be composed of a far greater proportion of highly coloured hydrophobic acids compared to the relatively un-coloured hydrophilic acids that were more dominant at the intact site, catchment waters may actually be easier to treat using existing techniques; as due to their lower levels of solubility, hydrophobic compounds are more easily removed at low pH.

Objective 3: Assess the spatial and temporal variability of the colour – carbon relationship, and thus the suitability of using colour as a proxy for true DOC determination.

A strong association between DOC concentration and water colour was identified in the blanket peat soil waters from Oughtershaw, with samples exhibiting a correlation coefficient of 0.88. However, the colour – carbon relationship was found to vary significantly between peat layers, land managements, and through time. This is thought to be a result of modifications to processes such as microbial decomposition and mineralisation pathways; hydrological transport/routing; and carbon sources and availability, all of which are known to have profound effects on the carbon forms available.

Consequently, the use of spectrophotometric analysis as an indirect method of DOC determination has been challenged, for although there is a significant and strong correlation between water colour and DOC, it was found that the use of a single regression equation resulted in the miscalculation of DOC concentrations by as much as 50 % as it did not take into consideration the fact that the fraction of coloured DOC components could vary by as much as 40 %. Furthermore, the ability of spectrophotometric techniques to measure low concentrations of DOC is ambiguous, as depending on the calibration used, and thus the value of the intercept, the minimum amount detectable varied greatly and was found to be as high as 10.32 mg Cl^{-1}. As the spectrophotometric determination of DOC in soil water solutions generally has little discriminatory power to distinguish between carbon fractions it is considered unsuitable for making accurate predictions regarding the DOC flux in such environments.

Objective 4: Establish the effect of drainage and drain blocking on DOC production potential, within the soil profile of an upland blanket peat.

It was found that the majority of the variation in peat-forming processes and subsequent DOC and colour production observed between the three land management practices can be explained by the variations in the height of the water table. Rates of microbial activity and thus DOC production at the intact site were generally limited by the high levels of surface saturation associated with a water table that was found to reside within the top 10 cm of the peat for 80 % of the time. Meanwhile, an elevated DOC production potential at the drained site was found to occur in response to a significantly lower water table and the associated de-watering of soil pores, which resulted in the upper soil layers being exposed for at least 65 % of the time. It is thought that this water table drawdown and greater level of oxidation resulted in the stimulation of pivotal degrading enzymes, with rates of microbial activity found to be enhanced by 33 % relative to the intact site, which corresponds well with the 35 % increase in DOC and colour values.

Drain blocking was successful in reducing DOC concentrations and the level of water discolouration due to a reduction in DOC production potential in response to the water table restoration and the re-saturation of the surface layers, whereby the amount of time the upper 10 cm of soil was aerated had reduced to 43 %. Accordingly, this resulted in a significant reduction in the rate of microbial activity, with values found to be reduced by nearly 50 % relative to the drained site, which corresponds well with the 49 % reduction in DOC. However, the rate of microbial activity, organic matter content and level of DOC produced were also lower than those observed at the intact site. This indicates that although there has been a significant amount of degradation of the surface layers, there is no evidence that an enzyme-latch reaction is sustained at the blocked site following re-wetting (Freeman *et al.* 2001b).

Objective 5: Determine the effect of drainage and drain blocking on the principle hydrological controls of runoff production, and thus DOC and colour transportation, within the soil profile of an upland blanket peat.

Water flow paths and runoff production in the blanket peat soils of Oughtershaw were influenced by water table depth. At the intact site, because the water table generally remains close to peat surface throughout the year it is likely that a high proportion of runoff occurs over the soil surface as overland flow (OLF); and due to the high rates of surface hydraulic conductivity, it is likely to be dominated by saturation-excess OLF rather than infiltration-excess OLF. Any water that does manage to infiltrate into the soil is likely to travel through free draining macropores, as the proportion of pores >1mm in diameter contributing to subsurface flow was high at 74 %. This suggests that water movement through and across the intact site is relatively rapid, which relates well with the flashy hydrological regime often reported for undisturbed blanket peat soils. Furthermore, because both OLF and macropore flow have relatively limited contact with the soil matrix and decompositional products, these hydrological processes are thought to exert a limited effect on water quality with respect to the flux of DOC and coloured waters.

In contrast, the lowering of the water table by nearly 10 cm at the drained site and the greater level of aeration of the surface layers reduced the level of surface saturation, which caused a reduction in the generation of OLF. As such, a greater volume of water is likely to be drawn down into the soil body relative to the intact site. In addition, however, the reduced level of overburden initiated a sequence of events that appears to have resulted in the subsidence and compaction of the upper soil layers, which increased the bulk density of the soil and ultimately reduced the degree of macroporosity. Therefore, as well as increasing the volume of water flowing through the soil body, it appears that drainage also results in a greater proportion of the water travelling through smaller meso- and micropores within the peat matrix. This would increase both the residence time of soil waters and the surface area over which they flow, which would result in percolating waters having a far greater level of interaction with decompositional products, enhancing their mobility within the soil.

A successful water table restoration at the blocked site resulted in a greater level of surface saturation and OLF generation relative to the drained site. However, the water table was lower and exhibited a greater degree of variability than that observed at the intact site, indicating that the volumetric changes associated with drainage may have permanently altered the structural and infiltration properties of the peat, and thus the manner in which water is stored. It is thought the smaller pore size distribution at the blocked site reduces the availability of water in the unsaturated zone due to the higher matrix potential, resulting in seasonal water deficits having far greater influence on the water table. The reduced level of macroporosity and build up of decompositional products in response to a lowered water table suggests that the initial response to water table restoration may have been a flush of DOC/colour and the preferential loss of the more labile components, as evident by the higher C/C ratio. Nonetheless, once the store of material became depleted, DOC and colour levels were significantly reduced relative to the intact site due to i) a reduction in production potential in response to the degradation of organic matter and a reduction in microbial activity; and ii) a slower rate of accumulation due to the elevated soil water interactions and porewater flushing initiated by the enhanced rate of subsurface flow through the soil matrix.

8.4. DATA LIMITATIONS AND FUTURE RESEARCH RECOMMENDATIONS

The data presented in this thesis are clearly applicable to the blanket peat soils of the Oughtershaw catchment. This is not to say that the results will not apply to other blanket peat deposits. Although it is clear that peatland drainage and subsequent water table restoration may bring about a range of impacts, the ultimate response of an individual peatland will depend on the nature of the individual soil properties that vary on a site-specific basis. Therefore, further study is clearly required in order to determine whether the same processes operate in other drained and restored blanket peat catchments at both a national and international scale.

In addition, two key areas were identified in which the methods of analysis may also be limiting factors. The first involved the use of spectrophotometric techniques to determine the composition of DOC in soil waters, which used measures such as the E4/E6 and C/C ratios to discriminate between the different DOC fractions and differentiate between refractory and labile components. Although this method proved highly effective, its lack of specificity means that absorbance data are not quantitative for solutions that contain complex mixtures of organic compounds. However, characterising the individual DOC components at a molecular scale is a complex task that requires a specialist analytical approach, and given the number of samples collected and the fact that this type of analysis is time consuming, labour intensive and expensive, such a rigorous method of approach was thought to be beyond the scope of this thesis.

The second limitation occurred in response to the method of Gammelgaard *et al.* (1992) which was undertaken in order to measure and compare rates of microbial activity across the three land managements. This method of analysis involved the spectrophotometric determination of INT-Formazan concentrations and incurred a significant degree of interference due to the release of the coloured humic substances characteristic of peat soils. Although a range of measures were applied to try and improve the efficiency of the technique and remove the interference, the low level of precision meant that some of the differences observed between sites proved to be insignificant when tested at the 95 % confidence level. Therefore, although this method of approach helped decipher the key biological processes involved in DOC and colour dynamics in drained and restored blanket peat, there is clearly a need for further research and methodological development.

The results presented in the preceding chapters of this thesis also identified several key areas of interest in which future investigation would greatly improve our current understanding of the processes operating in blanket peat soils. The recommended areas for research are as follows:

1. To distinguish between the short- and long-term impacts of drain blocking on DOC and colour dynamics, and to identify whether or not it is ever possible for a drained blanket peat to be fully restored.

2. To determine how the individual process modifications associated with drainage and drain blocking impact on species diversity with respect to variables such as surface vegetation and stream/soil water biota.

3. To quantify the effects of drainage and blocking on the type of DOC released by monitoring changes to its molecular composition, and thus identifying its likely source and subsequent decomposition pathway.

4. To link changes in DOC concentration and composition to additional carbon release pathways, such as CO_2 and CH_4 production and release.

5. To establish the effects of a far wider range of environmental and climate change scenarios on the composition and bioavailability of DOC.

8.5. CONCLUDING REMARKS

The results presented in this thesis offer new insight into the intimate processes controlling DOC and colour dynamics in blanket peat soils, and the impact of water table disturbance in the form of drainage and drain blocking on their prevalence. This will ultimately help improve our predictions made with respect to future climate and environmental change scenarios in these sensitive wetland ecosystems. In addition, this thesis provides land owners and policy makers with the evidence they require for initiating future peatland restoration works, as drain blocking is shown to be a highly effective technique for reducing DOC release and the level of water discolouration in a drained blanket peat catchment, and thus has potential applications to be used to improve the storage potential of a valuable terrestrial carbon sink and ameliorate several water quality issues currently prevailing in these upland environments. This research has also identified several key processes influential to the nature of the colour – carbon relationship that is prominent in peatland catchments, which will no doubt enhance the accuracy of future water quality monitoring programmes and fluvial carbon budget research that use water colour as a proxy for true DOC determination.

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APPENDIX 1

THE RESULTS OF A VEGETATION ASSESSMENT CARRIED OUT BY THE ENVIRONMENT AGENCY ON A BLANKET PEAT HILLSLOPE AT OUGHTERSHAW. SOURCED FROM MASTEL (2002).

Quadrat A: SD:83919,81824	This quadrat was located on the slope and supports an area of blanket bog with smaller areas of *Juncus effusus* mire to the south-west and centre-east. *Trichophorum cespitosum* is the most abundant species followed by *Eriophorum vaginatum, Deschampsia flexuosa, Sphagnum palustre, S. recurvum* and *Polytrichum commune.* Grazed *Vaccinium myrtillus* is frequent to abundant. Flatter areas have frequent to abundant *Molinia caerulea* and frequent small *Erica tetralix.* With reduced grazing and blocked grips, the outlook for this area of blanket bog is positive. Within this quadrat two unfavourable vegetation conditions were recorded: **1.** Dwarf shrub cover is unfavourable being less than 5% **2.** The graminoid cover is unfavourable being greater than 75% The other conditions listed under 'criteria' on the form for this quadrat are all favourable. *Calluna* is not regenerating by layering and the *Calluna* present is within the pioneer and building and early mature stage cover a negligible area. There is evidence of heavy grazing, with the widespread invasion by *Deschampsia flexuosa,* however the amount of *Eriophorum* spp is widespread and abundant and there is no trampling damage to *Sphagnum* hummocks or carpets, indicating only light grazing. Moderate grazing indicators include patchy *Sphagnum* carpets; local grazing of *Calluna vulgaris*; the amount of grazed *Vaccinium myrtillus* shoots; and negligible areas of trampled bare ground, paths and enhanced hagging. The graminoid cover in this quadrat is greater than 75%. Species present include abundant *Deschampsia flexuosa,* frequent *Molinia caerulea,* occasional *Nardus stricta, Agrostis stolonifera, Anthoxanthum odoratum* and *Festuca ovina* and scarce *Holcus lanatus* and *Holcus mollis.* The shrub species present within this quadrat are frequent *Vaccinium myrtillus,* occasional *Calluna vulgaris* and *Rubus chamaemorus,* locally frequent *Erica tetralix* and scarce *Vaccinium oxycoccos.* There is also abundant *Eriophorum vaginatum.*

APPENDIX 2

THE RESULTS OF A VEGETATION ASSESSMENT CARRIED OUT BY THE ENVIRONMENT AGENCY ON A BLANKET PEAT HILLTOP AT OUGHTERSHAW. SOURCED FROM MASTEL (2002).

<table>
<tr><td>Quadrat B:

SD:84091,81337</td><td>This was located at the top of the slope and supports lightly grazed blanket bog with blocked grips, presently dominated by graminoid but with moderately high cover of mosses; predominantly Sphagnum palustre and Polytrichum commune and low growth of abundant Vaccinium myrtillus, Erica tetralix and Calluna vulgaris.

Within this quadrat two unfavourable conditions were recorded:

1. Dwarf shrub cover is unfavourable being between 5 –33%

2. The graminoid cover is unfavourable being greater than 75%.

The other conditions listed under ‘criteria’ on the condition assessment form for this quadrat are all favourable.

Calluna is regenerating by layering and the Calluna present is within the building and early mature stage, covering less than 1% of the area.

There is evidence of heavy grazing with the invasion of the area by Deschampsia flexuosa and of moderate grazing with only patchy areas of Sphagnum, the presence of trampled bare ground and the presence of the Calluna growth form ‘topiary’.

The graminoid cover in this quadrat is greater than 75%. Species present include abundant Deschampsia flexuosa, frequent Molinia caerulea, occasional Nardus stricta and scarce Anthoxanthum odoratum.

The dwarf shrub species present within this quadrat include abundant Vaccinium myrtillus, frequent Erica tetralix and scarce Empetrum nigrum and Vaccinium oxycoccos.

There is also locally frequent Eriophorum angustifolium and abundant Eriophorum vaginatum.</td></tr>
</table>

APPENDIX 3

THE RESULTS OF A SOIL AND VEGETATION ASSESSMENT CARRIED OUT BY THE ENVIRONMENT AGENCY ON A DRAINED BLANKET PEAT AT OUGHTERSHAW. SOURCED FROM MASTEL (2002).

Location	Depth (m)	Description	von Post Grade
Camm Farm	GL – 0.03	Green and brown spongy fibrous PEAT	H1
Quadrat 1:	0.03 – 0.13	Black amorphous PEAT with some rootlets	H6
Upper Open	0.13 – 0.27	Brown amorphous PEAT with some rootlets	H6
	0.27 – 0.47	Brown amorphous PEAT with occasional rootlet	H9
Camm Farm	GL – 0.04	Green and brown spongy fibrous PEAT	H1
Quadrat 2:	0.04 – 0.12	Black amorphous PEAT with some rootlets	H6
Upper Fenced	0.1 – 0.60	Brown amorphous PEAT with some rootlets	H6
Camm Farm	GL – 0.04	Green and brown spongy fibrous PEAT	H1
Quadrat 3:	0.04 – 0.13	Black amorphous PEAT with some rootlets	H6
Lower Open	0.13 – 0.40	Brown amorphous PEAT with some rootlets	H6
Camm Farm	GL – 0.04	Green and brown spongy fibrous PEAT	H1
Quadrat 4:	0.04 – 0.14	Black amorphous PEAT with some rootlets	H6
Lower Fenced	0.14 – 0.47	Brown amorphous PEAT with some rootlets	H6

The quadrat area is dominated by *Deschampsia flexuosa*, *Eriophorum vaginatum*, *Molinia caerulea* and *Trichophorum cespitosus* with occasional *Festuca ovina*. Also present is abundant *Vaccinium myrtillus*, occasional *Galium saxatile* and sparse *Erica tetralix*. Bryophytes are dominated by *Sphagnum palustre*, *S. recurvum*, Polytrichum *commune* and occasional *Hypnum jutlandicum*, *Racomitrium lanuginosum* and *Dicranum sp.*

APPENDIX 4

THE RESULTS OF A SOIL AND VEGETATION ASSESSMENT CARRIED OUT BY THE ENVIRONMENT AGENCY ON A DRAIN-BLOCKED BLANKET PEAT AT OUGHTERSHAW. SOURCED FROM MASTEL (2002).

Location	Depth (m)	Description	von Post Grade
Swarthghyll Farm Quadrat 1: Upper Open	GL – 0.03	Grass and moss	H1
	0.03 – 0.09	Green and brown fibrous PEAT	H4
	0.09 – 0.48	Dark brown amorphous PEAT with some rootlets	H7/8
Swarthghyll Farm Quadrat 2: Upper Fenced	GL – 0.08	Spongy fibrous PEAT	H3
	0.08 – 0.15	Brown pseudo fibrous PEAT	H4
	0.15 – 0.5	Black amorphous PEAT with some rootlets	H5
Swarthghyll Farm Quadrat 3: Lower Open	GL – 0.07	Green and brown fibrous PEAT	H1
	0.07 – 0.13	Soft black brown amorphous PEAT with some rootlets	H7
	0.13 – 0.66	Soft brown fibrous PEAT with some rootlets	H4
Swarthghyll Farm Quadrat 4: Lower Fenced	GL – 0.07	Spongy fibrous PEAT	H3
	0.07 – 0.27	Soft black amorphous PEAT with some rootlets	H9/10
	0.27 – 0.50	Very soft brown amorphous PEAT with many rootlets	H7/8

The quadrat area is dominated by *Eriophorum vaginatum* with a abundant *Festuca ovina* and *Molinia caerulea* and small quantities of *Anthoxanthum odoratum*. Also present is abundant *Narthecium ossifragum* and *Galium saxatile*, occasional *Juncus squarrosus* and *Trichophorum cespitosus* and rare *Carex nigra, Drosera rotundifolia, Erica tetralix, Luzula multiflora, Potentilla erecta* and *Vaccinium myrtillus*. Bryophytes include abundant *Polytrichum commune* and *Sphagnum palustre* and occasional *Dicranum* sp.